PB91-125732

Characterization and Treatment of Wastes from Metal-Finishing Operations

PEI Associates, Inc., Cincinnati, OH

Prepared for:

Environmental Protection Agency, Cincinnati, OH

Nov 90

U.S. Department of Commerce
National Technical Information Service
NTIS

PB91-125732

EPA/600/2-90/055
November 1990

CHARACTERIZATION AND TREATMENT OF WASTES FROM METAL-FINISHING OPERATIONS

by

PEI Associates, Inc.
Cincinnati, Ohio 45246

EPA Contract No. 68-03-3389

Project Officer

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before complet

1. REPORT NO. EPA/600/2-90/055	2.	3. PB91-125732
4. TITLE AND SUBTITLE CHARACTERIZATION AND TREATMENT OF WASTES FROM METAL-FINISHING OPERATIONS		5. REPORT DATE November 1990 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) PEI Associates, Inc.		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS 11499 Chester Road Cincinnati, Ohio 45246		10. PROGRAM ELEMENT NO. D109 11. CONTRACT/GRANT NO. 68-03-3389
12. SPONSORING AGENCY NAME AND ADDRESS Risk Reduction Engineering Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED 10/86 - 9/89 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Project Monitor: Ronald J. Turner (513) 569-7775; FTS 684-7775

16. ABSTRACT

This Report is a Summary of Project Activities related to bench-and-pilot-scale Treatment of Electroplating Wastes scheduled for RCRA Land Disposal Restrictions (F006, F007, F009, F019).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Cyanide Heavy Metals	Chemical Oxidation Wet-Air-Oxidation Stabilization	

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED 20. SECURITY CLASS *(This page)* UNCLASSIFIED	21. NO. OF PAGES 128 22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The EPA is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report is a summary of project activities related to the bench- and pilot-scale treatment of various electroplating wastes scheduled for land disposal ban. Treatment technologies discussed in this report include alkaline chlorination, wet-air oxidation, ultraviolet light/ozonation, electrolytic oxidation, stabilization/solidification, and metals precipitation. Some of the performance data generated from these technology evaluations were used in the development of waste code-specific treatment standards for the land disposal restrictions program.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) include specific provisions restricting the land disposal of RCRA hazardous wastes. The purpose of these HSWA provisions is to minimize the potential of future risk to human health and the environment by requiring treatment of hazardous wastes prior to their land disposal. The EPA's Office of Research and Development (ORD) was responsible for treating several electroplating and metal-finishing waste codes and providing performance data in support of the development of treatment standards for the Land Disposal Restrictions Program.

This report summarizes the project activities associated with the characterization and treatment of some metal-finishing wastes. Information and data are presented on the waste generators' manufacturing and wastewater treatment plant operations, the chemical composition of the untreated wastes, and performance data generated from bench- and pilot-scale testing. Treatment technologies discussed in this report include alkaline chlorination, wet-air oxidation, ultraviolet light/ozonation, electrolytic oxidation, stabilization/solidification, and metals precipitation. Conclusions are presented regarding the effectiveness of the various technologies in treating selected electroplating and metal-finishing wastes.

In addition to the project-related material, this report also presents a section on cyanide chemistry. Most of the wastes discussed in this report contain cyanide salts or complexed cyanide; therefore, this section provides a background of useful information on terminology, definitions, cyanide chemistry, stability and toxicity of cyanide compounds, and analytical methodologies.

An appendix to this report provides a summary of the land disposal restriction treatment standards for the electroplating and metal-finishing wastes discussed in the report.

This report summarizes work conducted under U.S. EPA Contract No. 68-03-3389 during the period December 1, 1986 to September 30, 1989.

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ACKNOWLEDGMENTS

This report was prepared by PEI Associates, Inc. (PEI), Cincinnati, Ohio, as part of the work conducted for the EPA Risk Reduction Engineering Laboratory (RREL) under Contract No. 68-03-3389, Work Assignment No. 2-1A. Mr. Ronald J. Turner of RREL's Hazardous Waste Treatment Branch was the EPA Technical Project Monitor.

Mr. William F. Kemner served as PEI's Project Manager, and principal authors of this report were Messrs. Michael M. Arozarena, Philip W. Utrecht, and Jeffrey A. Willis. The authors wish to thank Dr. Terrence D. Chatwin, President of Resource Recovery and Conservation Consultants for preparation of the cyanide chemistry section of the report. The authors would also like to acknowledge the input of the following individuals and companies involved in this study: Mr. Rodger Julin with Amerock Corporation, Mr. Mike Wismer with Metro Recovery Systems (formerly with Amerock Corporation); Mr. John B. Newman with Master Lock Company; Mr. Ralph D. Grotelueschen with John Deere and Company; Messrs. William J. Ziegler and Norman E. Levitin with Cyanokem; Mr. James M. Sproat with Ford Electronics and Refrigeration Corporation; Mr. Douglas K. Parker with Circle-Prosco, Inc.; Ms. Linda Baehr with Woodward Governor Company; Dr. William M. Copa, Dr. Tipton L. Randall, Mr. Richard W. Leimann, and Mr. Bruce L. Brandenburg with Zimpro Passavant, Inc.; and Dr. Richard H. Snow with IIT Research Institute.

SECTION 1

INTRODUCTION

1.1 BACKGROUND

The Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) include specific provisions restricting the land disposal of RCRA hazardous wastes. The purpose of these HSWA provisions is to minimize the potential of future risk to human health and the environment by requiring treatment of hazardous wastes prior to their land disposal. A major section of these amendments is the requirement for EPA to set treatment standards, which substantially reduce the likelihood of constituent migration, for all RCRA hazardous waste. The treatment standards are to be based upon the performance of the best demonstrated available technology (BDAT) to treat the waste. Once set by the EPA, these standards must be met before land disposal is allowed. The EPA's Office of Research and Development (ORD) was responsible for conducting treatability studies on several electroplating and metal-finishing wastes and providing performance data in support of the development of treatment standards for the Land Disposal Restrictions Program.

1.2 REPORT OVERVIEW

This report summarizes the project activities associated with the characterization and treatment of some metal-finishing wastes scheduled for land disposal ban. Table 1 presents a listing of the waste codes under study, a description of the waste, the basis for listing, the waste generator(s), the technology scale, and the technology evaluated for each waste code. Information and data are presented on the waste generators' manufacturing and wastewater treatment plant operations, the chemical composition of the untreated wastes, and performance data generated from bench- and pilot-scale testing. Treatment technologies discussed in this report include alkaline chlorination, wet-air oxidation, ultraviolet light/ozonation, electrolytic oxidation, stabilization/solidification, and metals precipitation. Conclusions are also made as to the effectiveness of the various technologies in treating selected electroplating and metal-finishing wastes.

1.3 REPORT ORGANIZATION

Because most of the waste codes discussed in this report contain cyanide salts or complexed cyanide, Section 2 of the report seemed an appropriate place to present cyanide terminology, definitions, cyanide chemistry, stability and toxicity of cyanide compounds, and analytical methodologies. Section

TABLE 1. SUMMARY OF METAL-FINISHING WASTE CODES EVALUATED UNDER THE LAND DISPOSAL RESTRICTIONS PROGRAM FOR U.S. EPA's OFFICE OF RESEARCH AND DEVELOPMENT

EPA Hazardous Waste No.	Waste description	Basis for listing	Generators sampled	Technology/scale
F006	Wastewater treatment sludges from electroplating operations except from the following processes: 1) sulfuric acid anodizing of aluminum; 2) tin plating on carbon steel; 3) zinc plating (segregated basis) on carbon steel, 4) aluminum or zinc-aluminum plating on carbon steel; 5) cleaning/stripping associated with tin, zinc, and aluminum plating on carbon steel; and 6) chemical etching and milling of aluminum	Cadmium, hexavalent chromium, nickel, and cyanide (complexed)	Deere & Company Amerock Corp. Master Lock Co.	° Wet-air oxidation at bench-scale ° Stabilization/solidification at bench-scale
F007	Spent cyanide plating-bath solutions from electroplating operations	Cyanide (salts)	Amerock Corp.	° Wet-air oxidation at bench- and pilot-scale
F008	Plating bath sludges from electroplating operations where cyanides are used in the process	Cyanide (salts)	---	---
F009	Spent stripping and cleaning-bath solutions from electroplating operations where cyanides are used in the process	Cyanide (salts)	Master Lock Co.	° Ultraviolet light/ozonation at bench-scale
F011	Spent cyanide solutions from salt-bath pot cleaning from metal heat-treating operations	Cyanide (salts)	Woodward Governor Co.	° Electrolytic oxidation at full-scale ° Stabilization/solidification at bench-scale
F012	Quenching wastewater treatment sludges from metal heat-treating operations where cyanides are used in the process	Cyanide (complexed)	Woodward Governor Co.	° Electrolytic oxidation at full-scale ° Stabilization/solidification at bench-scale
F019	Wastewater treatment sludges from the chemical conversion coating of aluminum	Hexavalent chromium and cyanide (complexed)	Ford	° Wet-air oxidation at bench-scale

3 discusses four cyanide oxidation treatment technologies that were evaluated as potential BDAT for treating the wastes identified in Section 1. These technologies include alkaline chlorination, wet-air oxidation, ultraviolet light/ozonation, and electrolytic oxidation. Section 4 presents a brief discussion on metals precipitation of oxidized waste streams, and Section 5 discusses stabilization/solidification of Waste Codes F006, F011, and F012. Section 6 presents the results and conclusions obtained from the engineering site visits, bench- and pilot-scale tests, and stabilization/solidification tests. Finally, the Appendix presents a summary of the first-third and second-third land disposal restriction treatment standards for the electroplating and metal-finishing waste codes discussed in the report.

SECTION 2

CYANIDE CHEMISTRY, ANALYSIS, AND TOXICITY

TERMINOLOGY

The characterization of cyanide species falls into four general categories: 1) analytical methods, 2) ionic structure, 3) strength of the cyanide-metal complex bond, and 4) compound solubility.

The cyanide terms that relate to analytical procedures include free, weak-acid-dissociable (WAD), amenable, and total. The free cyanide definition relates to the measurement of cyanide anions, CN^-, and molecular hydrogen cyanide (HCN) in the solution. The definition of WAD cyanide is based on an ASTM analytical procedure for measuring the free cyanide and cyanide-metal complexes that are easily dissociated into free cyanide. The definition of amenable cyanide is based on an analytical procedure (EPA 1987, ASTM 1981) that was developed to determine cyanide species amenable to alkaline chlorination treatment. Although the total methods were designed to measure all cyanide species in solution, as pointed out in Ingersoll et al. (1983), some total cyanide methods are only partially successful in achieving this goal. For example, the most widely accepted methodology for analyzing total cyanide does not analyze for tightly bound cobalt, gold, or some platinum group complexes. More recent methods have been able to measure the cyanide from all species studied in the investigation (Ingersoll et al. 1983).

The cyanide relating to ion structure is described as simple and complex cyanides. The simple cyanide dissociates into the cyanide anion, CN^-, and the complex cyanide dissociates into a cyanide-metal anion [i.e., $Fe(CN)_6^{3-}$]. The terms based on the strength of the complex bond are the dissociable, nondissociable, and the WAD cyanides. Cyanide is also characterized by its solubility. These cyanides are defined simply as insoluble and soluble cyanides. Because these cyanide definitions are overlapping, they have resulted in some confusion. For example, cuprous cyanide and cupric cyanide [CuCN and $Cu(CN)_2$] are both simple and insoluble cyanides; however, potassium cuprocyanide [$KCu(CN)_2$] is also soluble, complex, amenable, dissociable, and a WAD cyanide. In addition, all of the species that are dissociable result in a portion of the cyanide occurring as a cyanide ion, CN^-, in the solution. Each of these definitions is discussed in the following subsections, and examples are given of specific cyanide species that fall into each category to help clear this confusion.

Free Cyanide

The term "free cyanide" is the sum of cyanide anions (CN^-) and hydrogen cyanide (HCN), which are the two most toxic cyanide species. In aqueous

solution, the HCN forms a weak acid with a dissociation constant of 4.365×10^{-10} at 20°C (Broderius 1974). The interrelationship between volatile hydrogen cyanide and the cyanide ion can be shown by the hydrolysis reaction:

$$CN^- + H_2O \rightarrow HCN + OH^-$$

As shown in Figure 1, The formation of free cyanide (either HCN or CN^-) depends on the solution pH. At a pH of 9.36, the concentration of HCN and CN^- are equal. Below a pH of 7 the free cyanide is essentially all HCN, and above a pH of 11 the free cyanide is all CN^-.

Weak-Acid-Dissociable Cyanide

Weak-acid-dissociable cyanide (WAD) refers to free cyanide and cyanide-metal complexes that are readily dissociated into free cyanide ions. This cyanide term is also described by an analytical procedure, which is defined by the ASTM in D-2036-81 Method C (ASTM 1982). This method is not sensitive to sulfide or thiocyanate interferences. Because it determines free and readily dissociable cyanide-metal complexes, the method results in a cyanide measurement that is more indicative of the solution toxicity due to cyanide than that due to total cyanide.

Examples of WAD cyanide species include CN^-, HCN, $Cu(CN)_2^-$, $Zn(CN)_4^{2-}$, and $Ni(CN)_4^{2-}$.

Amenable Cyanide

Amenable cyanide CN(A) refers to those cyanide species amenable to removal by alkaline chlorination. This method is based on analyzing for total cyanide before and after treatment with chlorine. This procedure is described in ASTM D-2036-81 Method B and SW-846 Methods 9010 and 9012 (EPA 1986). The alkaline chlorination oxidizes all cyanide-metal complexes except the iron complexes. Hence, the value should be similar to that in the WAD cyanide analysis.

Examples of amenable cyanide, CN(A), species are CN^-, NaCN, $Cu(CN)_2^-$, $Zn(CN)_4^{2-}$, and $Ni(CN)_4^{2-}$.

Total Cyanide

Total cyanide, CN(T) refers to all the cyanide groups in a sample regardless of the cyanide-metal complex, if any. The total cyanide value, however, is typically defined as the result of the analytical procedure, which may not include all cyanide-metal complexes. The total cyanide method generally used (the reflux mineral acid distillation) analyzes for all of the CN^- groups in the sample, including the cyanide-metal complexes (except cobalt, gold, and some of the platinum group metals). This method is defined in ASTM D-2036-81 and EPA's SW-846 Methods 9010 and 9012.

Examples of CN(T) are CN^-, NaCN, $Zn(CN)_4^{2-}$, and $Fe(CN)_6^{4-}$. The $Co(CN)_6^{4-}$ is an example of a total cyanide species that is not included in

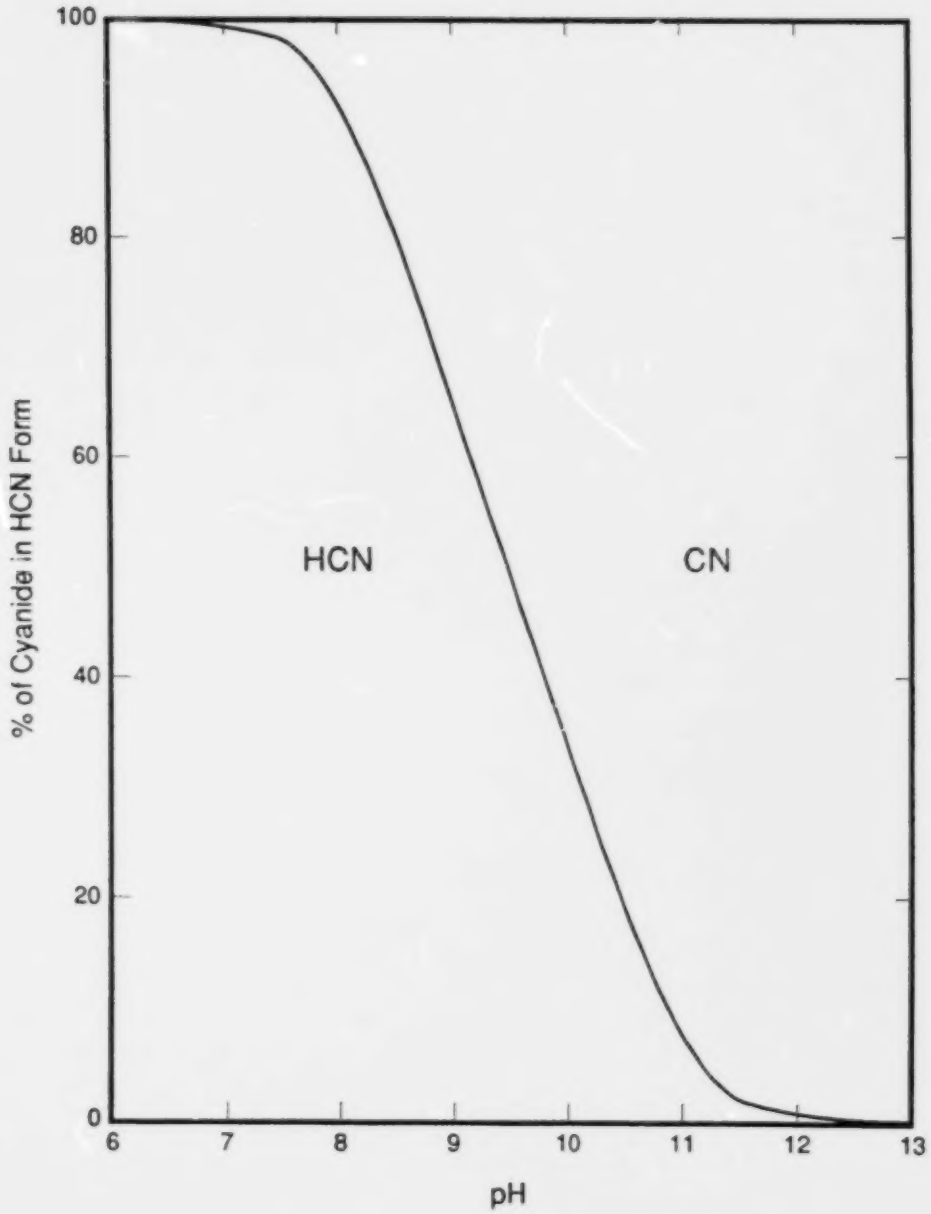

Figure 1. Relationship between HCN and CN with pH.

all total cyanide analyses. This element is discussed further under Analytical Methods presented later in this section.

Simple Cyanide

"Simple cyanide" denotes a compound in which cyanide combines with a single cation and does not form a cyanide complex. Simple cyanides are represented by the formula $A(CN)_x$, where A is an alkali (sodium, potassium, ammonium) or metal, and x, the valence of A, represents the number of cyanide groups present in the molecule. The solubilities for the simple cyanides vary widely. Soluble compounds, particularly the alkali cyanides, ionize to release cyanide ions according to the following equation:

$$A(CN)_x \text{ <---> } A^{+x} + xCN^-$$

Examples of simple cyanides are NaCN, $Ca(CN)_2$, and $Ni(CN)_2$ (insoluble).

Complex Cyanide

"Complex cyanides" is a compound in which the cyanide is complexed with a metal cation and results in a complex cyanide-metal anion on dissolution of the substance. The complex alkali-metallic cyanides are represented by the general formula $A_yM(CN)_x$, where A is the alkali, and y is the number of alkali ions. M is the heavy metal (i.e., iron, cadmium, copper, nickel, silver, zinc, or others) and x is the number of CN groups. The value of x is equal to the valence of A times y plus the valence of the heavy metal. The soluble complex cyanides dissociate to release the complex cyanide-metal ion $M(CN)_x^{yw-}$, where w is the oxidation state of A, rather than the CN^- ion. Thus, when they are dissolved in water, they ionize as shown below.

$$A_yM(CN)_x \text{ <---> } yA^{+x} + M(CN)_x^{yw-}$$

Examples of complex cyanides include $Na_4Fe(CN)_6$, $K_3Fe(CN)_6$, $K_2Cu(CN)_3$, $NaCu(CN)_2$, and $K_4Co(CN)_6$.

Dissociable Cyanide

The cyanide-metal complex anion stability depends on the metal cation with which it is associated. Zinc, cadmium, and copper are less stable and partially dissociated into the metal cation ard CN^-. Other complexes, particularly the iron, gold, and cobalt, are very stable; however, even tightly bound iron-complex anions can dissociate to release the cyanide (CN^-) ion in the presence of UV radiation or very strong acids (Broderius and Smith 1980, Sharpe 1976, and Moggi et al. 1966). All complex cyanides dissociate to free cyanide to some degree, as illustrated by the following reaction for chromium:

$$Cr(CN)_6^{3-} \text{ <---> } Cr^{3+} + 6\ CN^-$$

Examples of dissociable cyanide species include $Cu(CN)_2^-$, $Zn(CN)_4^{2-}$, and $Ni(CN)_4^{2-}$.

Nondissociable Cyanide

As was stated earlier, all cyanide complexes are dissociable to some degree. Hence, "nondissociable cyanide" is only a relative term used to describe cyanide complexes that are highly stable, such as $Co(CN)_6^{4-}$, $Au(CN)_4^-$, and the platinum group metals, and do not readily dissociate into free cyanide.

Soluble Cyanide

"Soluble cyanide" is defined as cyanide compounds or complexes that are soluble in aqueous solutions. The major utility of cyanide in a commercial sense is derived from its capacity to complex or chelate with metals (transition and precious) to form soluble cyanide-metal compounds. Consequently, it is not unusual that many of the cyanide compounds are soluble. Table 2 lists the solubilities of a number of cyanide compounds.

Insoluble Cyanide

"Insoluble cyanide" is defined as cyanide compounds insoluble in aqueous solutions. These compounds fall into two general categories: the relatively insoluble simple cyanides, such as $Zn(CN)_2$, CuCN, AgCN, and $Ni(CN)_2$; and the insoluble ferrocyanide and ferricyanide compounds, which are listed in Table 3. The insoluble simple cyanide complexes may be soluble in cyanide solutions. For example, copper is present in an assemblage as:

$$CuCN \quad \text{(insoluble)}$$

$$CuCN + CN^- \quad <---> \quad Cu(CN)_2^- \quad \text{(soluble)}$$

$$Cu(CN)_2^- + CN^- \quad <---> \quad Cu(CN)_3^{2-} \quad \text{(soluble)}$$

$$Cu(CN)_3^{2-} + CN^- \quad <---> \quad Cu(CN)_4^{3-} \quad \text{(soluble)}$$

The complexes form in a stepwise fashion. As the cyanide ion concentration increases, the higher cyanide complexes become the stable species; hence, the insoluble CuCN combines with CN^- to form a soluble $Cu(CN)_2^-$ and then the higher cyanide complexes.

Cyanate

Cyanide can be oxidized by ozone, hydrogen peroxide, sodium hypochlorite, or sulfur dioxide and air to produce cyanate and, subsequently, ammonium ion and carbon dioxide. Aerobic bacterial degradation of cyanide also produces cyanate. A review of cyanide treatment systems by Huiatt et al. (1983) discusses these treatment methods in greater detail (also, see Section 3). The oxidation of cyanide by peroxide is presented here:

$$CN^- + H_2O_2 \quad <---> \quad CNO^- + H_2O$$

TABLE 2. SOLUBILITIES OF METAL-CYANIDE COMPOUNDS[a]

Compound	Name	Solubility, mole/liter	Reference[b]
AgCN	Silver cyanide	1.64×10^{-6} (20°C)	1
$Cd(CN)_2$	Cadmium cyanide	1.51×10^{-5} (18°C)	1
$Co(CN)_2$	Cobaltous cyanide	3.77×10^{-4} (18°C)	1
CuCN	Cuprous cyanide	2.90×10^{-5} (18°C)	1
$Hg(CN)_2$	Mercuric cyanide	3.68×10^{-1} (20°C)	1
$Hg_2(CN)_2$	Mercurous cyanide	1.79×10^{-6} (25°C)	1
$Ni(CN)_2$	Nickel cyanide	5.35×10^{-4} (18°C)	1
$Zn(CN)_2$	Zinc cyanide	4.90×10^{-5} (18°C)	1
$K[Ag(CN)_2]$	Potassium dicyanoargentate(I)	1.3 (20°C)	2
$K_2[Cd(CN)_4]$	Potassium tetracyanocadmate(II)	1.1	2
$K_3[Cr(CN)_6]$	Potassium hexacyanochromate(III)	1 (20°C)	2
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate(III) (ferricyanide)	1 (4°C)	2
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II) (ferrocyanide)	0.7 (12°C)	2

[a]Source: Ingersoll et al. 1983.

[b] References:

1. Kunz et. al 1978
2. Sillen and Martell 1971

TABLE 3. SOLUBILITIES OF FERROCYANIDES AND FERRICYANIDES[a]

Name	Formula	Solubility, g/liter T°C
Ammonium ferricyanide	$(NH_4)_3Fe(CN)_6$	Very soluble
Ammonium ferrocyanide	$(NH_4)_4Fe(CN)_6 \cdot 3H_2O$	Soluble
Barium ferrocyanide	$Ba_2Fe(CN)_6 \cdot 6H_2O$	1.7 g (15°C)
Cadmium ferrocyanide	$Cd_2Fe(CN)_6 \cdot xH_2O$	Insoluble
Calcium ferrocyanide	$Ca_2Fe(CN)_6 \cdot 12H_2O$	868 g (25°C)
Cobalt ferrocyanide	$Co_2Fe(CN)_6 \cdot xH_2O$	Insoluble
Copper (I) ferricyanide	$Cu_2Fe(CN)_6$	Insoluble
Copper (II) ferricyanide	$Cu_3[Fe(CN)_6]_2 \cdot 4H_2O$	Insoluble
Copper (II) ferrocyanide	$Cu_2Fe(CN)_6 \cdot xH_2O$	Insoluble
Iron (II) ferricyanide	$Fe_3[Fe(CN)_6]_2$	Insoluble
Iron (III) ferricyanide	$FeFe(CN)_6$	---
Iron (II) ferrocyanide	$Fe_2Fe(CN)_6$	Insoluble
Iron (III) ferrocyanide	$Fe_4[Fe(CN)_6]_3$	Insoluble
Lead ferricyanide	$Pb_3[Fe(CN)_6]_2 \cdot 5H_2O$	Slightly soluble
Manganese (II) ferrocyanide	$Mn_2Fe(CN)_6 \cdot 7H_2O$	Insoluble
Nickel ferrocyanide	$Ni_2Fe(CN)_6 \cdot xH_2O$	Insoluble
Potassium ferricyanide	$K_3Fe(CN)_6$	330 g (4°C)
Potassium ferrocyanide	$K_4Fe(CN)_6 \cdot 3H_2O$	278 g (12°C)
Silver ferricyanide	$Ag_3Fe(CN)_6$	0.00066 (20°C)
Silver ferrocyanide	$Ag_4Fe(CN)_6 \cdot H_2O$	Insoluble
Sodium ferricyanide	$Na_3Fe(CN)_6 \cdot H_2O$	189 g (0°C)
Sodium ferrocyanide	$Na_4Fe(CN)_6 \cdot 10H_2O$	318.5 g (20°C)
Strontium ferrocyanide	$Sr_2Fe(CN)_6 \cdot 15H_2O$	500 g
Thallium ferrocyanide	$Tl_4Fe(CN)_6 \cdot 2H_2O$	3.7 g (18°C)
Tin (II) ferricyanide	$Sn_3[Fe(CN)_6]_2$	Insoluble
Tin (II) ferrocyanide	$Sn_2Fe(CN)_6$	Insoluble
Tin (IV) ferrocyanide	$SnFe(CN)_6$	Insoluble
Zinc ferrocyanide	$Zn_2Fe(CN)_6$	Insoluble

[a]Source: Weast 1988.

This reaction is followed by the hydrolysis of the cyanate to ammonium and carbonate ions.

$$CNO^- + 2\ H_2O \text{ <---> } NH_4^+ + CO_3^{2-}$$

STABILITY AND TOXICITY OF THE VARIOUS FORMS OF CYANIDE

Common Forms of Cyanide

The common forms of cyanide are 1) free cyanide as cyanide anion (CN^-) and hydrogen cyanide (HCN); 2) simple cyanides [i.e., CuCN, KCN, $Hg(CN)_2$, etc.]; and 3) complex cyanides [i.e., $Fe(CN)_6^{4-}$. $Cu(CN)_3^{2-}$, etc.], which also include ferro- and ferricyanide precipitates [i.e., $Fe_2Fe(CN)_6$]. Table 4 presents further delineation as to cyanide-metal complex stabilities and solubilities of these forms of cyanide and gives typical examples. The simple cyanides, by definition, form no complexes. The soluble cyanides dissolve to form metal cations and the cyanide anion. The soluble complex cyanides dissolve into metal cations and cyanide-metal complex anions. The cyanide-metal anion can then further dissociate into cyanide anions and the metal cation in a stepwise fashion, as shown here:

$$Cu(CN)_3^{2-} \text{ <---> } Cu(CN)_2^- + CN^-$$

$$Cu(CN)_2^- \text{ <---> } Cu(CN) + CN^-$$

$$CuCN \text{ <---> } Cu^+ + CN^-$$

Hence, the cyanide-metal complexes also result in free cyanide in the solution. The concentration of the free cyanide depends on the solution pH and the strength of the cyanide-metal bond, as measured by the dissociation constant present for some complexes (Table 5).

TABLE 4. CYANIDE FORMS, COMPLEX STABILITY, AND SOLUBILITY

Common cyanide forms	Complex cyanide stability	Solubility	Examples
Free	No complexes	Soluble	CN^-, HCN
Simple	No complexes	Soluble	NaCN, $Ca(CN)_2$
	No complexes	Insoluble	CuCN, $Zn(CN)_2$
Complex	Dissociable	Soluble	$Zn(CN)_4^{2-}$, $Cu(CN)_2^-$
	Nondissociable	Soluble	$Fe(CN)_6^{4-}$, $Co(CN)_6^{4-}$
	Nondissociable	Insoluble	$Fe_3[Fe(CN)_6]_2$

TABLE 5. STABILITY CONSTANTS OF METAL-CYANIDE COMPLEX IONS

Complex ion	Stability constant	Reference[a]
$Cr(CN)_6^{3-}$	10^{33}	1
$Cr(CN)_6^{4-}$	10^{21}	1
$Fe(CN)_6^{4-}$	$10^{35.4}$	1
	10^{47}	2
$Fe(CN)_6^{3-}$	10^{52}	3
$Co(CN)_6^{4-}$	10^{50}	1
$Co(CN)_6^{3-}$	10^{64}	3
$Ni(CN)_4^{2-}$	10^{30}	1
	$10^{31.1}$	3
$Pd(CN)_4^{2-}$	10^{42}	1
$Pt(CN)_4^{2-}$	10^{40}	1
$Cu(CN)_2^{-}$	$10^{23.9}$	1
$Cu(CN)_3^{2-}$	$10^{29.2}$	1
$Cu(CN)_4^{2-}$	$10^{30.7}$	1
$Cu(CN)_4^{3-}$	$10^{30.3}$	3
	$10^{20.9}$	4
$Ag(CN)_3^{2-}$	$10^{21.9}$	1
$Au(CN)_2^{-}$	10^{37}	1
$Au(CN)_4^{-}$	10^{85} (estimate)	1
$Zn(CN)_4^{2-}$	10^{21}	3
	$10^{16.7}$	1
$Cd(CN)_4^{2-}$	10^{19}	3
	$10^{16.9}$	1
$Hg(CN)_4^{2-}$	10^{39}	3
	$10^{\cdot 41.1}$	3
$Mn(CN)_6^{4-}$	$10^{9.7}$	1

[a] References:
1. Sharpe 1976.
2. Broderius 1973.
3. Kunz, G. G., J. P. Casey, J. E. Huff 1978.
4. L. S. Sillen and A. E. Martell 1971.

Cyanide Toxicity--Free Cyanide

Free cyanide is highly toxic to man and animals. The toxicity and metabolism of free cyanide are well documented, particularly as they relate to fish (Sax 1984, Doudoroff 1980, Ingersoll 1983, and U.S. EPA 1985). For example, a hydrogen cyanide concentration of 0.3 mg/liter (270 ppm) in air is immediately fatal to humans. Cyanide toxicity to fish is even more acute; concentrations as low as 0.1 ppm in water are fatal to a broad range of fish (Ingersoll 1983).

Free cyanide uptake by man and animals occurs through inhalation, ingestion, or skin absorption. Absorption via membranes and skin occurs readily, and the blood system rapidly distributes the cyanide throughout the body. The free cyanide binds strongly to iron, copper, and sulfur, key constituents of many enzymes and proteins important in life processes. The principal compound affected is cytochrome oxidase, an enzyme contained within the body cells and essential to the cell utilization of oxygen. This inactivation of the oxidase results in cellular asphyxiation and tissue death.

Cyanide Toxicity--Complexed

The toxicity of the various metal-cyanide complexes is attributable almost solely to the concentration of free cyanide in equilibrium with the complex salt. The toxicity of the simple cyanide compounds depends on their solubility or their ability to form ionic or free cyanide. The toxicity of complex cyanide is a function of the solubility and stability of the complex cyanide-metal ion. For example, weakly bound complexes such as zinc and cadmium cyanide are much more toxic than iron or cobalt complexes. Ferrocyanide complex is approximately 1/200 to 1/300 (Sax 1984) times less toxic to rats than is free cyanide. In fact, most investigators (Deichmann and Gerande 1969) consider iron cyanide nontoxic. Excellent presentations on cyanide toxicity can be found in Towill et al. (1978), Huiatt et al. (1983), and Doudoroff (1980).

Cyanide-Metal Complex Stability

The stability of the cyanide-metal complex anion depends on the metal cation with which it is associated. Zinc, cadmium, and copper are relatively unstable and partially dissociate into the metal cation and CN^-. Other complexes, especially the iron, gold, and cobalt complexes, are very stable; however, even tightly bound iron-complex anions can dissociate to release the cyanide (CN^-) ion in the presence of UV radiation or very strong acids. All complex cyanides dissociate in aqueous solution to free cyanide to some degree, as illustrated by the following reaction for chromium:

$$Cr(CN)_6^{3-} \leftrightarrow Cr^{3+} + 6\ CN^-$$

The stability constant (K_s) for this cyanide complex is defined as follows:

$$K_s = \frac{[Cr(CN)_6^{3-}]}{[Cr^{3+}][CN^-]^6} = 10^{33}$$

The inverse of the stability constant is the dissociation constant (K_d):

$$K_d = 1/K_s = 10^{-33} \text{ [for } Cr(CN)_6^{3-}\text{]}$$

Table 5 lists equilibrium stability constants for a number of complex cyanide ions.

The dissociation constant 4.365×10^{-10} for the dissociation reaction of hydrogen cyanide can be used to determine the concentration of CN^- as a function of pH:

$$HCN <--> H^+ + CN^-$$

A decrease in the pH drives the dissociation reaction forward by removing the cyanide ion. Therefore, by controlling the pH of the solution, some of the cyanide complexes can be totally dissociated into free cyanide. An increase in temperature results in an acceleration of the dissociation rate. These mechanisms are used in the acid reflux distillation methods to dissociate cyanide-metal complexes to form volatile HCN so it can be trapped and measured.

The complex alkali-metallic cyanides are represented by the general formula $A_yM(CN)_x$, where A is the alkali, and y is the number of alkali ions. M is the heavy metal (i.e., iron, cadmium, copper, nickel, silver, zinc, or others) and x is the number of CN groups. The value of x is equal to the valence of A times y plus the valence of the heavy $M(CN)_x$ rather than the CN^- ion. Thus when they are dissolved in water they ionize as follows.

$$A_yM(CN)_x <--> yA^{+x} + M(CN)_x^{-yw}$$

where w is the oxidation state of A.

The complex cyanide-metal ion may then undergo further dissociation and release cyanide ions as shown here.

$$M(CN)_x^{-yw} <--> CN^- + M(CN)_{x-1}^{-yw+1}$$

$$M(CN)_{x-1}^{-yw+1} <--> CN^- + M(CN)_{x-2}^{-yw+2}$$

Metal-cyanide complex ions may be considered as the soluble products of the reaction between the corresponding insoluble simple cyanide and excess cyanide ion.

Another aspect of cyanide-metal complex chemistry is the formation of insoluble double-metal cyanide precipitates. This reaction has been used successfully to remove free cyanide from solutions by the formation of ferric ferrocyanide, $Fe_4(Fe(CN)_6)_3$, or other transition metal ferrocyanide precipitates (Hendricksen and Daignault 1973).

$$4\ Fe^{3+} + 3\ Fe(CN)_6^{4-} \text{ <---> } Fe_4\ [Fe(CN)_6]_3\ (ppt)$$

ANALYTICAL METHODS

Four general catagories of cyanide analytical methods are commonly used: 1) total cyanide, 2) cyanide amenable to chlorination, 3) WAD cyanide, and 4) free cyanide.

These techniques are typically designed for an aqueous waste or leachate; however, the acid reflux/distillation method used for total, amenable, and WAD analyses has also been applied to soils and sludges. Because the corrosive action of the acid on the solid phase may release compounds that could interfere with the cyanide analysis, this approach should be used with caution. In situations where the solid could cause cyanide interferences, 100 grams of the solid may be leached with 1000 ml of 2 normal NaOH for 24 hours and then filtered and the leachate analyzed for cyanide species.

Total Cyanide, CN(T)

Total cyanide includes all inorganic species containing the CN radical, including free cyanide and simple and complex cyanide-metal compounds. The following paragraphs briefly describe total cyanide procedures.

Acid Reflux/Distillation--

Acid reflux/distillation (SW-846 Methods 9010 and 9012, ASTM D-2036-81 Method A) at a pH of 2 is the most commonly used method for total cyanide analysis. A catalytic agent, $MgCl_2$, is added to the sample before distillation to ensure breakdown of the tightly bound iron cyanide complexes. Hydrogen cyanide volatilized during the distillation is collected in an alkaline absorbing solution. The free cyanide can then be measured by any of the accepted techniques, such as titration, colorimetry, or specific ion electrode (presented later in this section). Unfortunately, this procedure has the following problems: it is quite susceptible to interferences from thiocyanate, sulfides, thiosulfate and other sulfur compounds; it is affected by nitrite, nitrate, and oxidizing agents; and it does not measure all cyanide species as discussed previously.

Current published versions of the various standard cyanide procedures have presented modified procedures (i.e., use of phosphoric acid rather than sulfuric acid, additions of ascorbic acid to eliminate oxidizing agents, and the addition of cadmium carbonate to remove the sulfides) that reduce these interferences. The particular interferences of thiocyanate and sulfide compounds, however, have made it difficult to compare data produced by various industries.

One modification developed by Knechtel and Conn (1981) has been designed to determine cyanide in the presence of thiocyanate. This is a modified version of the conventional acid reflux/distillation technique in which hydrochloric acid and hydroxylamine hydrochloride are the decomposition reagents. Cadmium chloride is added to the adsorber to precipitate any sulfide that is distilled over. Cyanide determinations after distillation are resolved by titrimetric or colorimetric methods, depending on the cyanide concentration. This method has been successfully applied to measure cyanide in process waters. Tartaric acid or phosphoric acid solutions have also been used successfully in place of sulfuric acid for samples that show thiocyanate interference.

Final analysis of the ionic CN^- obtained from distillation is commonly obtained by any of three methods: 1) titration, usually with $AgNO_3$; 2) colorimetry via the reaction of chloramine-T derivative of CN^- with a pyridine-barbituric acid; and 3) ion-selective electrode techniques using the method of known additions.

Automated Ultraviolet Digestion--

Automated Ultraviolet Digestion (SW-846 Method 9012) is being used by many laboratories to replace the catalysts in the decomposition of complex-metal cyanides in the total cyanide determinations (U.S. EPA 1979, Sekerka and Lechner 1976). Phosphoric acid is the recommended digesting solution, and the determination is performed with the Technicon Auto-analyzer. The method has a major advantage in terms of its automation, but it exhibits interferences from thiocyanates and sulfides. Broderius and Smith (1980) found that light with wavelengths less than 420 nm and 480 nm acts to decompose $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, respectively. Maximum absorption wavelengths are 330 nm for $Fe(CN)_6^{4-}$ and 330 and 420 nm for $Fe(CN)_6^{3-}$.

Ligand-Exchage--

Ligand-exchange, which is listed in a review by Ingersoll et al. (1983), is another method for measuring total cyanide. This process involves the use of ligands to aid the dissociation of the tightly bound cyano-metal complexes. Lead acetate is added to precipitate sulfides. The pH is maintained at 4.5, and the distillation time is reduced to 1/2 hour. The ligand used was a mixture of TEP and Tiron (1,2-dehydroxy-3,5-benzenedisulfonic acid). It uses high-temperature reflux distillation from acidic solutions of organic complexing agents. This process requires neither UV radiation nor strongly acidic solutions to decompose the complex iron cyanides.

Ion Chromatography--

Ion chromatography methods have been developed to determine total cyanide, WAD cyanide, and free cyanide. Much of this developmental work has been performed by Pohlandt-Watson (1984, 1986a) in South Africa. These methods are free from interferences and are quite precise. They have a limit of determination of 10 µg/liter. The total cyanide content was determined by ion chromatography after the strong metal-cyanide complexes had been resolved in hypophosphorous acid by ultraviolet irradiation of wavelengths shorter than 300 nm. The dissociation procedure (10 minutes) is faster than conventional distillation methods.

Amenable Cyanides, CN(A)

The cyanide amenable-to-chlorination method is based on the difference between two total cyanide determinations on a sample both before and after chlorination. One sample portion is analyzed for total cyanide. Another portion is treated with calcium or sodium hypochlorite at an alkaline pH for 1 hour, the chlorine residual is removed, and the solution is analyzed for total cyanide. The alkaline chlorination oxidizes all cyanides (except the iron complexes) as well as thiocyanate. The difference between the two total values is reported as cyanide amenable to chlorination.

Although this method is an accepted standard by the EPA and ASTM, it has an obvious problem--the result is only as good as the initial total cyanide value determination before chlorination. If the interferences, such as thiocyanate, are not eliminated or corrected, a low value could be obtained for cyanide amenable to chlorination because the alkaline chlorination removes thiocyanate. Using the phosphoric acid methodology for total cyanide where thiocyanate is a problem eliminates this interference, however.

The test work at the Wastewater Testing Center in Canada confirms that the iron cyanide complexes are not oxidized but that other metal complexes (such as copper, nickel, and cadmium) and free cyanide and thiocyanate are. When both process samples and synthetic solutions containing cyanide, iron, ferricyanide, and thiocyanate were used, the relative standard deviation for this method was about + or - 5 percent at levels of 2.5 mg/liter for the process sample and 0.2 mg/liter for the synthetic solution (Conn 1981).

Weak-Acid-Dissociable Cyanides (WAD)

The WAD method (ASTM D-2036 Method C) of cyanide determination and the cyanide amenable to chlorination, CN(A), analyses (ASTM D-2036 Method B) are both designed to measure free cyanide plus metal-cyanide complexes other than iron, cobalt, and gold. Because the CN(A) procedure requires two separate analytical procedures (one before and one after chlorination) that are subject to errors and interferences, many investigators use the ASTM Method C approach, CN(WAD).

The WAD cyanide procedure is a variation of one proposed by Roberts and Jackson (1971). A distillation is carried out in the same equipment and in the same manner as described for total cyanide but with different reagents in the distilling flask. The reagents used are an acetic acid-sodium acetate solution buffered at pH 4.5 and zinc acetate. The purpose of the zinc acetate is to prevent decomposition of any ferrocyanide present. At the Chemical Congress of the North American Continent held in Mexico City in 1975, it was indicated that this analytical procedure is capable of totally recovering cyanide from cadmium, copper, nickel, silver, and zinc complexes. No thiocyanate interference occurs with this method.

Free Cyanide

The free cyanide analysis is designed to measure the highly toxic species (i.e., the cyanide ion CN^- and the HCN molecule). Solvent extraction

or air sparging is used to separate the free cyanide from the process solution containing substances that could interfere with the analysis. These techniques are also used to measure the free cyanide trapped in the alkaline scrubber solution in the acid reflux/distillation method for total, amenable, and WAD cyanide.

Titration with colorimetry, silver nitrate, or ion-selective electrode techniques are typically used to measure free cyanide. Two other methods, gas and ion chromatography, have recently been developed. An ion chromatographic method for free cyanide, as well as for cyanide-metal complexes, was developed in South Africa by Pohlant-Watson (1984, 1986b). This method is particularly promising for both laboratory and process samples because it measures both thiocyanate and cyanate and is not subject to interference by these compounds.

Absorption Spectrophotometry--

The absorption spectrophotometry method is based on the formation of a colored molecular species of cyanide. The absorbed light in the solution is compared with a previously determined calibration plot. The cyanide concentration in the sample is then determined by comparison with the calibration data. Although various absorption compounds are used by different investigators, the most frequently used compound is the blue dye formed by treating cyanide with chloramine-T and then with an aqueous pyridine solution of bispyrazolone and 3-methyl-1-phenyl-5-pyrazolone. The detection limit is 0.5 µg in a 15-ml aqueous solution. The effective range is about 1 to 5 µg in a 25-ml aqueous solution. The relative standard deviation (RSD) of this method is approximately 2 percent. If the blue dye is concentrated by extraction into a small volume of organic solvent, greater sensitivity is obtained (American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1971). A modification of the pyridine-pyrazolone method has reduced the detection limit to 5 µg/liter cyanide.

Sulfides, heavy metal ions, fatty acids, substances that hydrolyze to give cyanide ions, and oxidizing agents that are likely to destroy cyanide during the distillation step interfere with the determination of cyanide by this method, but they can be eliminated or minimized by the appropriate treatments.

Absorption spectrophotometry is probably the most widely used technique for determining cyanide in concentrations of 1 mg/liter or less. Its accuracy is adequate for analysis of cyanide in natural waters as well as treated industrial effluents. It is also amenable to automation.

Volumetric Titrimetry--

Volumetric titrimetry can be used if the cyanide content of the alkaline distillate is sufficiently large, a minimum of 1 mg/liter (EPA 1979a). For example, silver nitrate combines with cyanide according to the equation:

$$2CN^- + AgNO_3 \text{ <--> } Ag(CN)_2^- + NO_3^-$$

One milliliter of 0.01 N silver nitrate is thus equivalent to 0.52 mg of cyanide ion. When the end point of the titration is reached, excess silver ions react with the indicator to produce a characteristic color change. A blank reagent value is then subtracted from the result.

The indicator, p-dimethyl-aminobenzalrhodanine, for the silver nitrate titration, is sensitive to about 0.1 mg/liter silver or about 0.05 mg cyanide. If a 500-ml sample is used, the minimum detectable concentration of cyanide by the titration technique is about 0.1 mg/liter. The RSD is about 2 percent for distilled samples that contain at least 1 mg/liter cyanide (American Public Health Association, American Water Works association, and Water Pollution Control Federation, 1971).

In summary, volumetric titration methods are simple and widely used in analyzing water samples and industrial effluents when the cyanide concentration is greater than 1 mg/liter. The use of simple equipment and a conventional laboratory procedure make this approach very attractive.

Ion-Selective Electrodes--

Ion-selective electrodes can be used to determine cyanide in certain industrial wastewaters. A specially designed electrode that contains a membrane of silver sulfide and silver iodide is used. When the electrode is immersed in a sample, iodide is released at the membrane surface in an amount proportional to the cyanide in the sample. The iodide is measured by the electrode and determines the electrode potential. Consequently, the electrode response follows the relationship,

$$E = E_x + S \log [CN^-]$$

where E = the electrode voltage, mV
$[CN]^-$ = the concentration of the cyanide ion
S = slope of the electrode response curve

Only free cyanide ions, CN^-, are detected; molecular hydrogen cyanide and cyanide-metal complexes do not activate the electrode. Thus, samples must be adjusted to pH greater than 11 before measurement to ensure that all free cyanide is present as cyanide ion. In addition, complexing cations such as nickel or copper must be sequestered with ethylenediaminetetra-acetic acid to free complexed cyanide prior to analysis. Sample color and turbidity do not interfere with the use of the cyanide-specific electrode. Time-consuming sample distillations are eliminated; consequently, this method is appropriate for direct field measurements as well as automated laboratory use.

The cyanide ion-selective electrode is slowly attacked by cyanide solutions, which leads to inaccuracies. The electrode is also continually subject to drift with time and requires frequent recalibration. Because sulfide deactivates the electrode, the electrode must not be immersed in sulfide-containing solutions.

In conclusion, although the ion-selective electrode determination of cyanide is attractive for selected application because sample preparation is usually eliminated and analyses are obtained speedily, it is also subject to drift and electrode attack that may cause analytical inaccuracies. The silver iodide membrane electrode is useful in the 10^{-3}- to 10^{-5}-M concentration range; above 10^{-3}-M cyanide, the electrode life is shortened by the cyanide attack of the electrode. The technique is amenable to automation, but strongly complexed metal ions must be limited by sample pretreatment.

Gas Chromatography--

Gas chromatography techniques readily distinguish various species of cyanide compounds. In general, hydrogen cyanide and other cyanide-containing compounds have different characteristic retention times in the chromatographic column and can be identified by this criterion. Hydrogen cyanide in an aqueous cyanide solution can be removed from the sample by air sparging, concentrated in a cold trap, and analyzed in chromatographic columns by using a nitrogen carrier gas and a flame ionization detector. Samples containing 1 µg/liter hydrogen cyanide are readily analyzed. The calibration curve is linear up to 2000 µg/liter (Claeys and Freund 1968).

In summary, the gas chromatographic method of determining cyanide is sensitive and precise. In addition, it can distinguish speciated forms of cyanide-containing molecules. These characteristics suggest its application for the analysis of cyanide from biological materials, gaseous and liquid effluents, and wastewaters. This technique is little used at present.

Ion Chromatography--

Ion chromatography methods have been developed to determine free cyanide. A simplified flow-injection technique has been developed by Pohlandt-Watson (1984, 1986b) that is suitable for the on-line determination of ionic cyanide in process solutions. This method uses a ion-selective electrode, and it improves the accuracy of the free cyanide determinations by ion-selective electrode. With this technique, 60 samples can be analyzed in 1 hour, with an RSD of 0.012 at the 100-mg/liter level.

The recently developed ion chromatographic method of determining free cyanide is rapid, sensitive, and precise. In addition, it can distinguish speciated forms of cyanide-containing ions. These characteristics recommend its application for the analysis of cyanide from gaseous and liquid effluents and wastewaters.

Analytical Interferences

Thiocyanate--

Thiocyanate ion interference, particularly when Cu_2Cl_2 catalyst is used, has been well documented (Barton 1978). The Cu_2Cl_2 catalyst causes the formation of cyanogen, $(CN)_2$, in the distillation flask. This volatile compound is hydrolyzed to CN^- and CNO^- in the alkaline scrubber, which results in low analysis for cyanide. Because of this problem and others, the ASTM procedure has been changed to use the $MgCl_2$ catalyst (ASTM 1981).

Thiocyanate is a well-recognized source of interference in several analytical procedures for total cyanide measurement. For example, the UV digestion methods for total cyanide require a determination of thiocyanate to calculate the amount of iron cyanide present. Thiocyanate also interferes with the calculation of cyanides amenable to chlorination. At the Chemical Congress of the North American Continent held in Mexico City in 1975, it was reported that artificially high values obtained after chlorination resulted in a negative value for amenable cyanides in samples with a high ratio of thiocyanate to free cyanides.

Sulfides--

Sulfides volatilized in the distillation flask as H_2S are trapped in the alkaline scrubber solution as HS^-. The HS^- can react with cyanide to form thiocyanates, which results in low cyanide analyses. Sulfides can also interfere with the titrimetric and electrolytic determinations (Clysters 1976). During storage, sulfides also slowly react with cyanides (especially at high pH) form thiocyanates, and reduce the cyanide values (ASTM 1981).

Nitrates, Urea, Glycine, and Others--

Nitrates, urea, glycine, and others can generate cyanide under test conditions and cause false positive readings even when no cyanide is present (Rapean et al. 1980). Other possible interferences include oxidizing agents, aldehydes, glucose, carbonates, fatty acids, and amino acids.

The ASTM (1981) method statement sums up the magnitude of the interference problem in the statement "It is beyond the scope of these methods to describe procedures for overcoming all of the possible interferences that may be encountered."

Storage--

Storage of the sample can also result in inaccuracies in the determination of cyanide. A clear filtered sample preserved by the addition of sodium hydroxide to a pH of 12 and stored in the dark at 4°C will be stable for at least 2 weeks. A pH of above 11 is essential to eliminate HCN volatilization. Storage in the dark will eliminate dissociation of iron cyanides by light. Samples containing solids are difficult to store, and adequate preservation cannot be guaranteed (Conn 1981). The preparation-analysis alternatives are either immediate analysis for cyanide or filtering the sample and elevating the pH to 12. Any sulfides in a sample should be removed by precipitation with lead carbonate before raising the pH for preservation. Also, if alkaline chlorination is used for cyanide destruction, any residual chlorine should be removed after chlorination.

SECTION 3

CYANIDE OXIDATION TREATMENT

This section presents an overview of the four cyanide oxidation treatment technologies included in this study: alkaline chlorination, wet-air oxidation, ultraviolet light/ozonation, and electrolytic oxidation.

ALKALINE CHLORINATION

General Description

Alkaline chlorination is the method the electroplating industry uses most often for detoxifying cyanide. This process can be used both to destroy free dissolved hydrogen cyanide and to oxidize all simple and many complex inorganic cyanides in wastewater.

The destruction reaction is a redox process in which one or more electrons are transferred from the cyanide complex to the oxidizing agent. The most commonly used oxidizing agents are chlorine or hypochlorite salt.

The reaction scheme for the destruction of cyanide by alkaline chlorination, which is carried out at ambient temperatures, is shown by the following (Alliance Technologies Corp. 1987):

$$CN^- + Cl_2 \rightleftharpoons CNCl + Cl^- \quad (1)$$

$$CNCl + 2OH^- \rightleftharpoons CNO^- + Cl^- + H_2O \quad (2)$$

$$2CNO^- + 4OH^- + 3Cl_2 \rightleftharpoons 6Cl^- + 2CO_2 + N_2 + 2H_2O \quad (3)$$

In the above reaction scheme, chlorine gas and hydroxide ion are used to oxidize cyanide to cyanate (CNO^-) and, ultimately, to carbon dioxide and nitrogen. Despite its higher cost, sodium hypochlorite (NaOCl) is often used to replace chlorine because of the dangers and high equipment costs associated with the use of chlorine.

Alkaline chlorination treatment of cyanide solutions is conducted in either one or two stages. Single-stage alkaline chlorination involves Reactions 1 and 2, in which cyanide is oxidized to cyanate. In two-stage

alkaline chlorination, the chemical reaction is taken one more step in which cyanate is oxidized to carbon dioxide and nitrogen (Reaction 3). The two-stage process is more commonly used by industry (Alliance Technologies Corp. 1987). In the two-stage process, the solution pH is first raised to 10 or higher. Hydrolysis of the cyanogen chloride ($CNCl$) complex is rapid and typically yields 80 to 90 percent completion to CNO^- within 2 minutes (reaction time depends on the composition of feed stream). The pH is then reduced to a range of 8.0 to 8.5, which allows for rapid oxidation of cyanate (Reaction 3). Generally, Reaction 3 requires between 30 minutes and 1 hour to ensure the complete destruction of cyanide. An alternative method for carrying out the two-stage process is to maintain a pH between 8.5 and 10 in a single tank to allow for the simultaneous completion of both stages (Alliance Technologies Corp. 1987; Cushnie 1985).

Single-stage alkaline chlorination carries out the reaction scheme only through the formation of cyanate, which is about 1000 times less toxic than cyanide (Sittig 1973). In areas where discharge of cyanate is allowed, industry will select single-stage alkaline chlorination because of its lower capital and operation and maintenance costs.

Overall reagent requirements for the complete destruction of cyanide (two-stage alkaline chlorination) are 6.8 lb of chlorine and 7.3 lb of caustic per pound of cyanide. Demonstration has shown, however, that a 10 percent excess of chlorine (8 lb Cl_2 per lb CN) is needed to destroy cyanide and to meet current effluent guidelines (Alliance Technlogies Corp. 1987 and Patterson 1985). Single-stage alkaline chlorination requires 3 lb of chlorine per pound of cyanide treated.

A continuous-flow alkaline chlorination system is designed to handle cyanide wastestream concentrations of 100 mg/liter or less at flow rates of 10 to 350 gal/min (flow rates are dependent on influent CN concentrations) (Alliance Technologies Corp. 1987). Optimum influent cyanide concentrations for continuous systems are less than 100 mg/liter. Wastestream cyanide concentrations of up to 2 to 4 percent, however, can be treated in the batch mode (Sittig 1973). Total cyanide levels of 0.5 mg/liter or less in the effluent can typically be reached if feed is below 1000 mg/liter CN and no stable inorganic complexes (i.e., iron, nickel, and zinc) are present in the wastestream (Sittig 1973).

Site Description--Master Lock

Master Lock Company in Milwaukee, Wisconsin, manufactures a variety of padlocks. Operations include forming, heat treatment, painting, assembly, and electroplating. Electroplating operations involve a total of six plating lines; five are barrel plating lines, and one is a rack plating line. The rack plating line is dedicated to Ni-Cr plating of hardened steel. The barrel plating lines include one line each for Cu-Ni plating of hardened and nonhardened steel, Cu-Ni plating of zinc die cast, chromating/stripping, Cd plating of lock bodies, and Cd plating of steel and zinc die cast internal parts. In the performance of these electroplating operations, Master Lock generates EPA Hazardous Waste Nos. F006, F007, F008, and F009. Annual gener-

ation rates of the individual wastes codes were not available. Treatment of these waste streams (except for F006) is provided by three onsite wastewater treatment systems, which are described in detail in the following paragraphs. The F006 is shipped offsite for stabilization/solidification and land disposal.

Wastewaters and sludges generated by Master Lock's six electroplating lines are treated in three onsite wastewater treatment systems: 1) a conventional wastewater treatment system, 2) a complexed wastewater treatment system, and 3) a batch wastewater treatment system. The conventional treatment system receives copper cyanide rinsewaters, alkaline cleaner wastewaters (F009) (cadmium plating lines only), cadmium cyanide rinse waters, acid rinse waters, chromating rinse water, and chrome plating rinse water. The conventional wastewater treatment system treats approximately 75,000 gal of wastewater and sludge per day. It consists of chromium reduction, single-stage alkaline chlorination, neutralization, flocculation, sedimentation, sand filtration, sludge thickening, and pressure filtration. Figure 2 is a flow schematic of the conventional wastewater treatment system.

The complexed wastewater treatment system receives washer rinse water and alkaline cleaner rinse water (except that from the cadmium plating lines), which may contain chelants. The complexed wastewater treatment system, which processes about 65,000 gal/day, consists of a series of two neutralization tanks to break the chelated metal bonds, followed by flocculation, sedimentation, sludge thickening, and pressure filtration. Master Lock indicated that the wastewaters treated in this system contain no cyanide. Figure 3 is a flow schematic of the complexed wastewater treatment system.

The batch treatment system receives spent alkaline cleaner bath solution (F009), spent nickel cyanide bath solution (F007), spent cadmium cyanide bath solution (F007), plating bath sludges (F008), cadmium stripping solutions (F009), and chromium stripping solutions (F009). The spent nickel cyanide bath solution is actually in the form of carbonate sludge. The spent solution is pumped to an outside tank that serves as a chiller to remove excess carbonate. The treated bath solution is returned to the plating lines. The nickel carbonate sludge (or residue) is pumped to the acid/chrome batch transfer station and then to the acid/chrome hold tank (Tank 29) for batch treatment. The spent cadmium cyanide bath solution, which is also in the form of carbonate sludge, is treated similarly. The cadmium carbonate sludge (or residue) is pumped to the alkaline/cyanide hold tank (Tank 25) for batch treatment. The batch treatment system treats about 1000 gal/day and consists of chromium reduction, two-stage alkaline chlorination, a sludge thickener, and a filter press. Figure 4 is a flow schematic of the batch wastewater treatment system.

Site Description--Amerock Corporation

Amerock Corporation in Rockford, Illinois, manufactures a wide variety of decorative hardware for homes. Amerock's product line consists primarily of brass-plated decorative hardware; however, they also perform copper, zinc, nickel, and chrome plating. Some of the raw materials that Amerock uses in

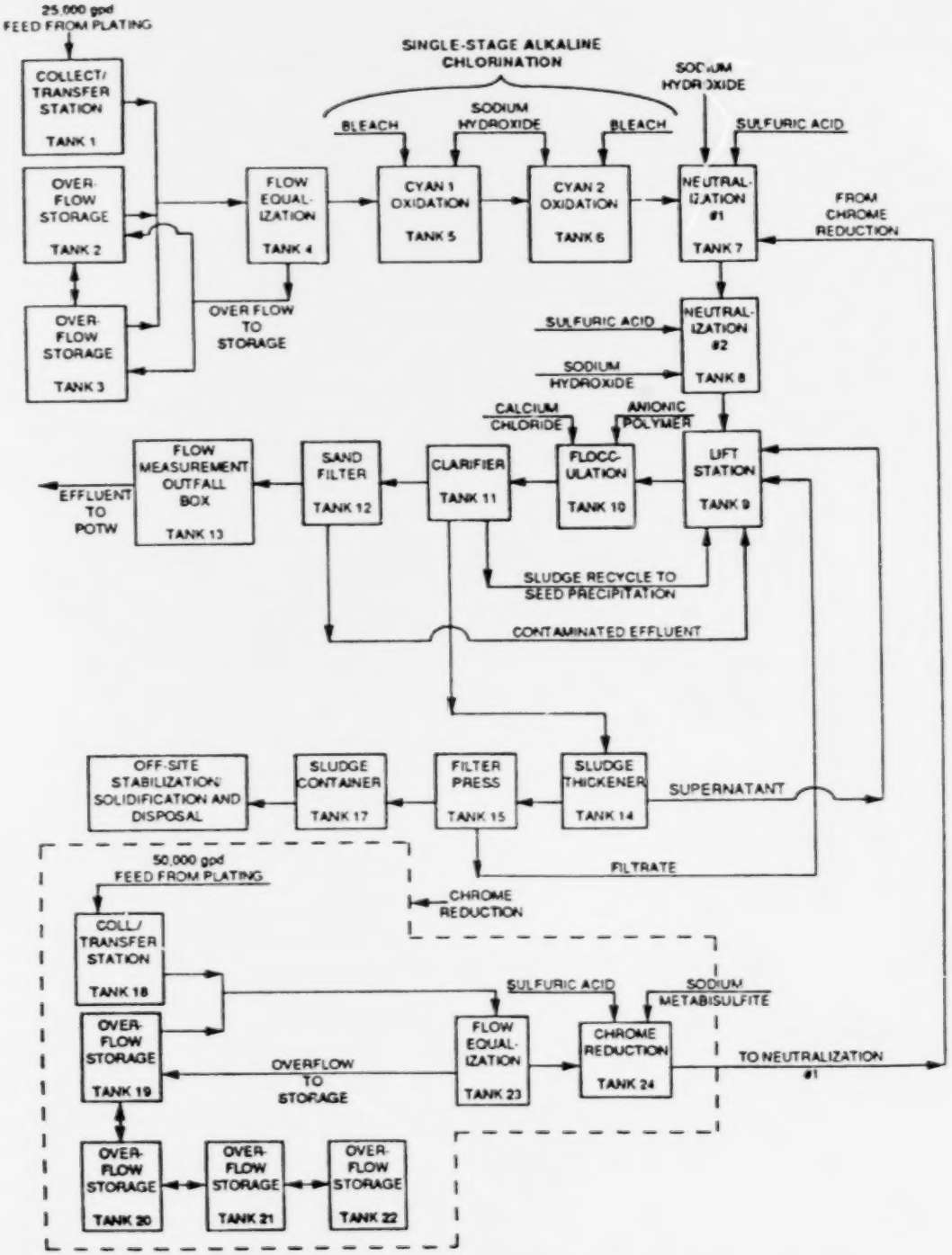

Figure 2. Schematic of Master Lock's conventional wastewater treatment system.

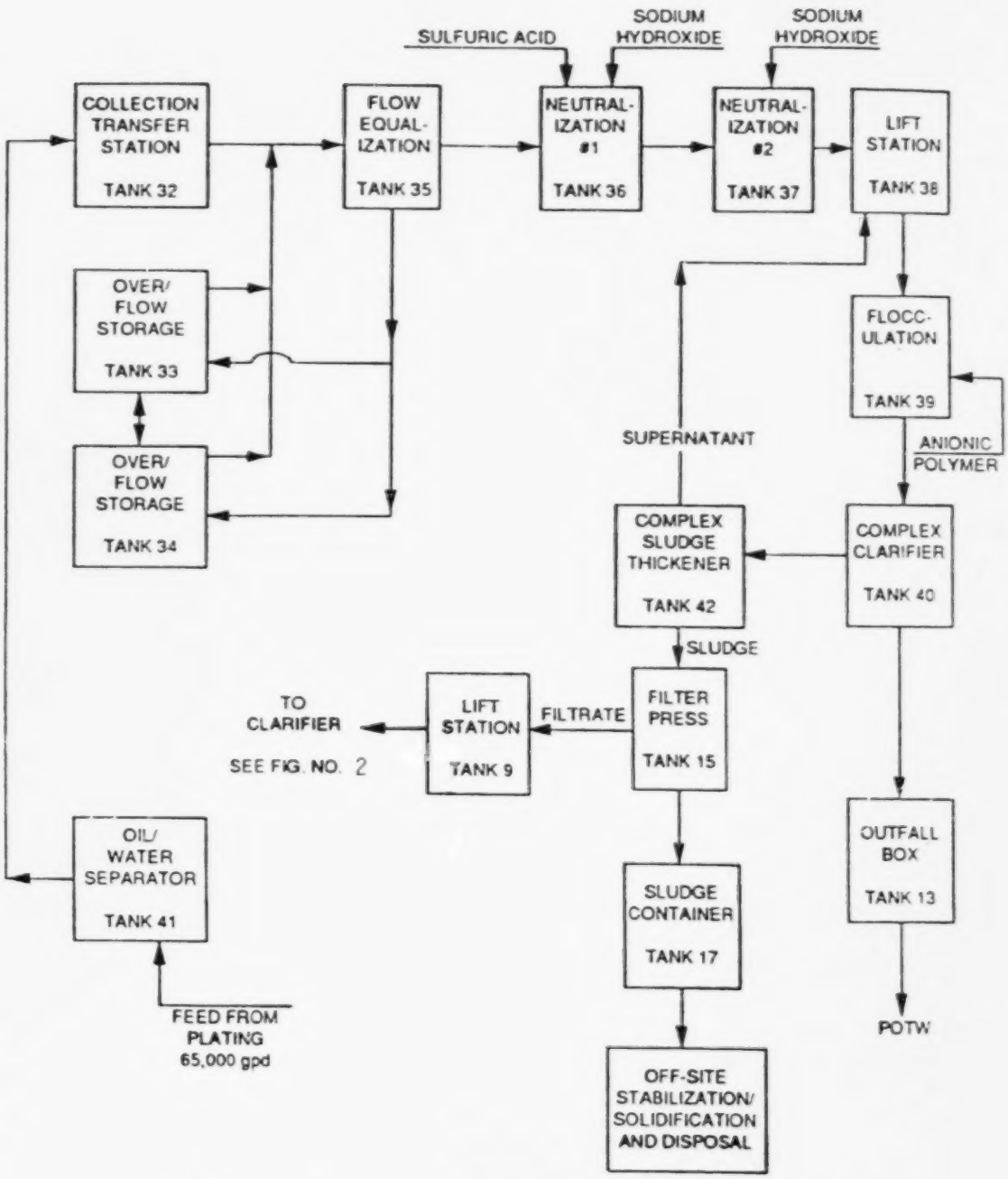

Figure 3. Schematic of Master Lock's complexed (chelated wastewaters) wastewater tretment process.

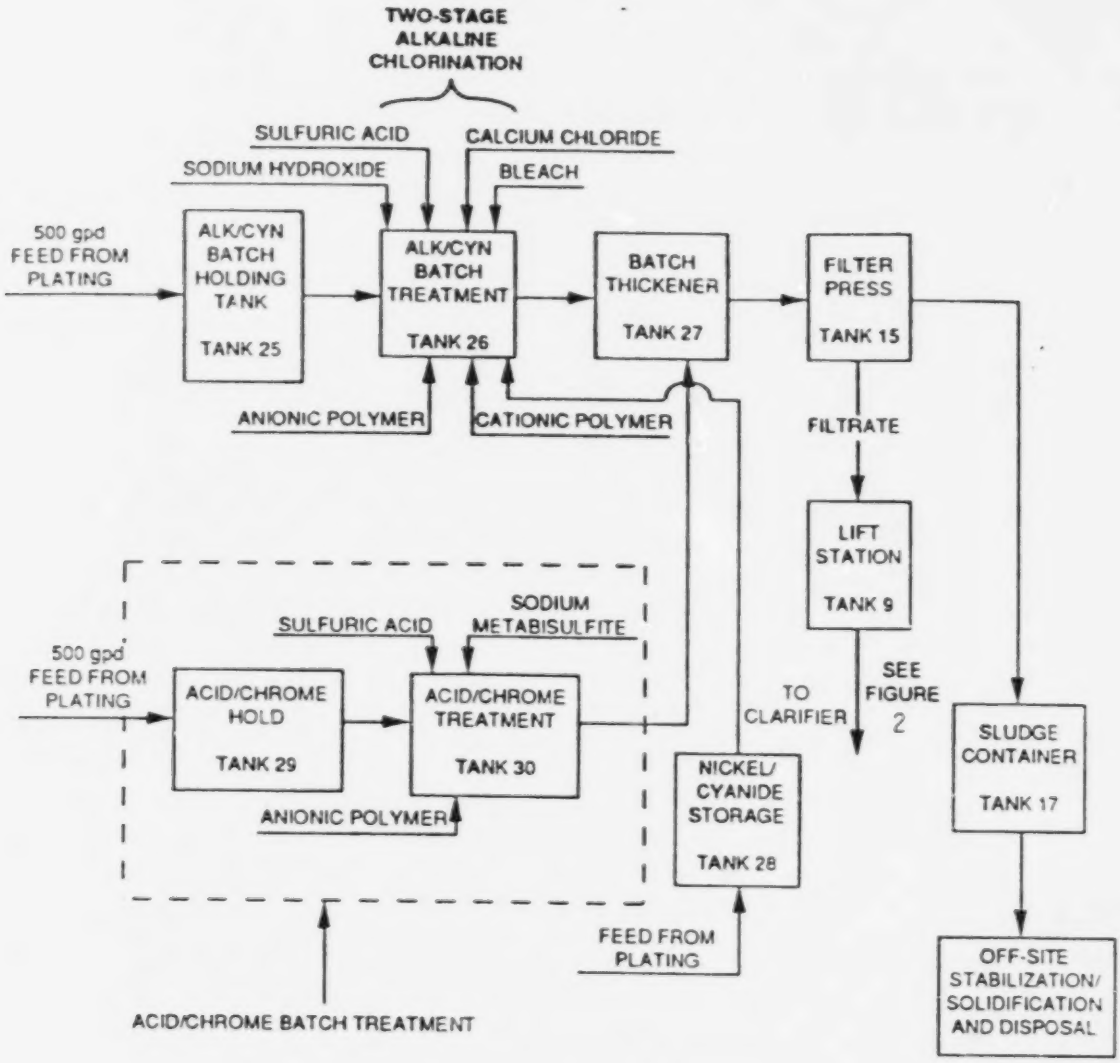

Figure 4. Schematic of Master Lock's batch wastewater treatment system.

support of their manufacturing operations include steel, zinc, and plastics. Production operations involve some 20 blanking processes, 20 molding and melting processes, 8 plastic molding machines, and 50 secondary processes (such as tapping). Finishing operations consist of electroplating, cleaning, antiquing, lacquering, and painting. Amerock's electroplating lines use both rack and barrel plating, but barrel plating accounts for about 70 percent of the products. In the performance of these electroplating operations, Amerock generates EPA Hazardous Wastes Nos. F006, F007, F008, and F009. Treatment of these waste streams (except for F006) is provided by onsite batch and continuous alkaline chlorination.

Wastewater and sludge generated by Amerock's electroplating operations are treated in an enclosed onsite wastewater treatment plant. The plant consists of three wastewater treatment lines, referred to by plant personnel as the batch cyanide treatment line, the continuous cyanide destruction line, and the continuous noncyanide precipitation line (Figure 5). Only the two cyanide treatment lines are discussed in this report.

Wastewater and sludge influent to the batch cyanide treatment line consists of F007, F008, and F009. Spent cyanide plating bath solutions (F007) at Amerock are discharged in batch quantities to an onsite chiller* (i.e, refrigeration unit), which reduces the carbonate concentration in the spent plating bath solution from 28 to 30 oz/gal to 12 to 15 oz/gal. This process generates a carbonate sludge that may contain 2 to 4 percent total cyanide. After refrigeration, the plating bath solution is returned to the plating line. Amerock does not dispose of its plating solutions in any way except for the small amount retained in the carbonate crystals. Amerock generates F008 only about three to four times a year.

In the batch cyanide treatment of wastes identified as F007, F008, and F009, wastewater and sludge are pumped to a 28,000-gal equalization tank. In the past, batch treatment took about 24 to 36 hours per batch; now the treatment cycle takes only about 7 hours because Amerock is diluting about 660 gal of raw waste with city water to a volume of about 2000 gal.

The wastewater is pumped from the equalization tank to a chlorination tank in which cyanide is oxidized to cyanate (first-stage chlorination) by the addition of sodium hydroxide and chlorine gas. After the batch retains a chlorine residual for at least an hour, sodium thiosulfate is added to remove this residual before the wastewater is pumped to the ammonia-stripping tank. The chlorine is removed prior to ammonia stripping so chlorine gas and ammonia are not released inside the treatment building. Chlorine also affects the settling characteristics of the sludge. Steam and air are injected into the ammonia-stripping tanks, and the vapors emitted from the tank are directed to a sulfuric stripping column for the removal of ammonia. Exit gas from the column is released to the atmosphere, and the column effluent

* Chillers or refrigeration units are commonly used in the electroplating business to remove excess carbonate that affects plating performance.

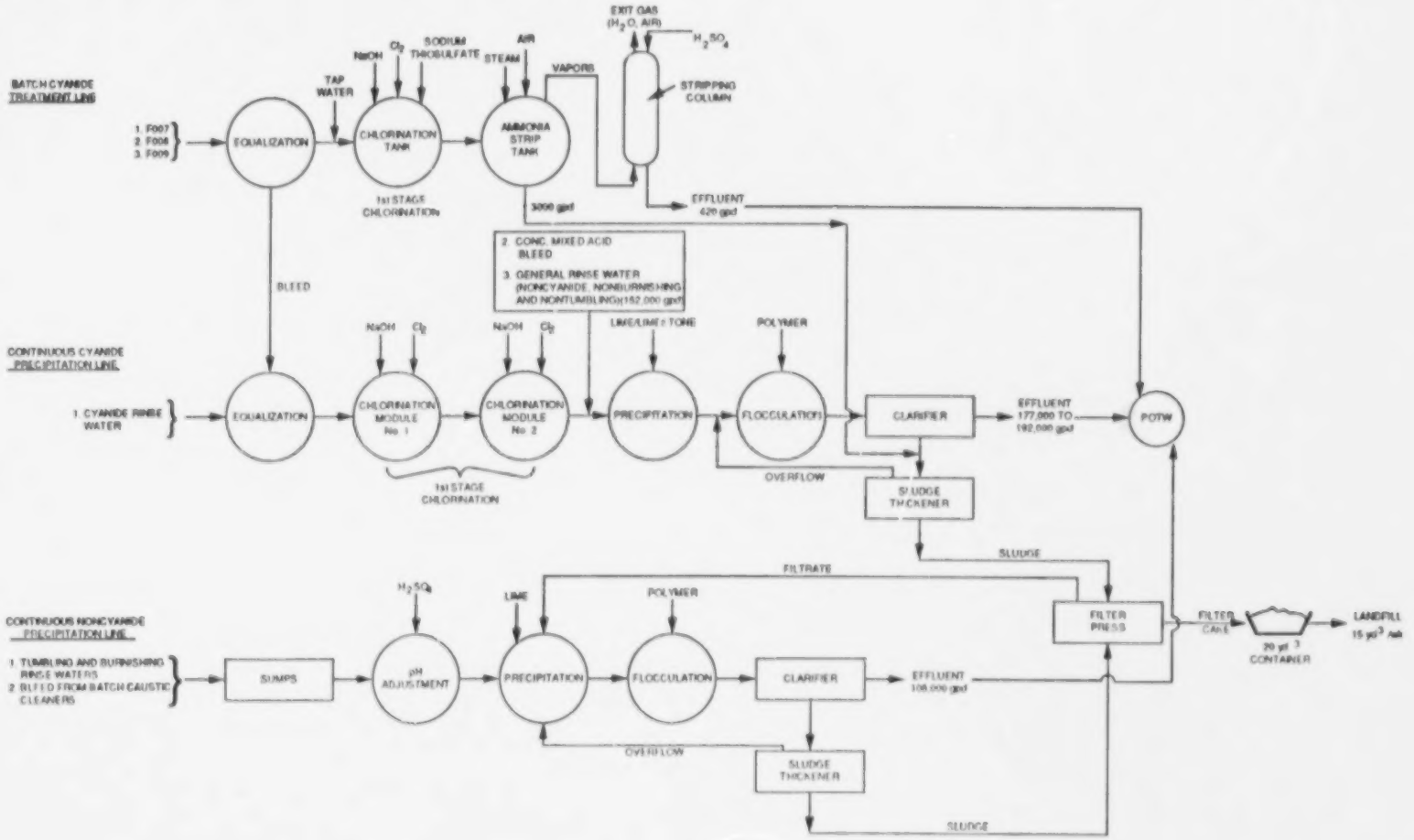

Figure 5. Wastewater treatment at Amerock Corporation.

(about 1 gal/min or 420 gal/day) is discharged to the POTW (Sanitation District of Rockford). Upon completion of the ammonia-stripping and cooling-cycle, the contents of the tank (about 3000 gal/day) are pumped to a sludge thickener.

The continuous cyanide precipitation line receives cyanide rinse waters and a bleed stream from the batch cyanide treatment line. After the chlorination modules, general rinse waters consisting of noncyanide, nonburnishing, and nontumbling wastewaters and concentrated mixed acid bleed are introduced. The equalization tank receives about 15,000 to 30,000 gal/day of cyanide-bearing wastewater for treatment. After equalization, the wastewater is pumped to a series of two alkaline chlorination modules, where cyanide is oxidized to cyanate (first-stage chlorination) by the addition of sodium hydroxide and chlorine. Just prior to the precipitation tank, 162,000 gal/day of general rinse waters enter the precipitation line. Lime and limestone are used for precipitation of heavy metals, followed by the addition of anionic polymer in the flocculation tank. After flocculation, the wastewater gravity feeds to a rectangular clarifer. Underflow from the clarifier and the discharge from the ammonia-stripping tank (batch cyanide treatment) are directed to a sludge thickener. Overflow from the thickener is returned to the flocculation tank, and the thickened sludge is pumped to a filter press. The filtrate is returned to the precipitation tank in the continuous noncyanide precipitation line, and the filter cake is collected in 20-yd^3 containers for landfill disposal. The continuous cyanide precipitation line treats and discharges to the publicly owned treatment works (POTW) about 177,000 to 192,000 gal of wastewater per day.

Site Description--CyanoKEM

CyanoKEM is a commercial hazardous waste treatment facility that receives industrial inorganic wastes, including acids, alkalis, and cyanide-bearing wastes. Typical wastes treated at CyanoKEM are cleaning solutions, stripping solutions, pickling liquors, and spent plating baths. The majority of the wastes treated at CyanoKEM are drummed wastes made up of combinations of salts, sludges, slurries, and liquids. Bulk liquids, including waste rinses and baths, are handled in 5000-gal or larger volumes. Cyanide-bearing wastes are oxidized with sodium hypochlorite under alkaline conditions to cyanate (first-stage chlorination). Treated wastes are clarified, and the effluent is discharged to the city of Detroit sewer system at a rate of about 50,000 gal/day. Stabilized, dewatered sludge is shipped to a hazardous waste landfill. CyanoKEM's wastewater treatment facility has a design capacity of 35 million gallons per year.

All bulk cyanide waste tankers are sampled and checked in the laboratory by fingerprint tests. If the tests show the waste to be acceptable and treatable, the load (normally up to 5000 gal) is discharged into one of the four 25,000-gal primary cyanide treatment tanks. If it is a predominantly simple cyanide, it may be isolated in a cyanide treatment tank (C-1 through C-4) and treated individually. The simple cyanide load, however, may be placed with another batch of simple cyanide waste in tanks C-1 through C-4

and treated as a combined batch to achieve proper dilution and optimum conditions for cyanide treatment. A batch of simple cyanide may be present as a bulk load or as a dissolved drum cyanide waste from a side tank (C-5 or C-6). Cyanide bulk loads are generated from a variety of metal plating and finishing operations. Typical examples are spent solutions of sodium, potassium, zinc, or cadmium cyanide baths.

Cyanide bulk loads that are shown to contain certain heavy metals are considered complex cyanides. These are unloaded into tanks C-1 through C-4 in a manner that keeps them separate from simple cyanide batches. Typical complex bulk cyanides contain dissolved and precipitated copper cyanides along with some nickel and/or iron cyanides.

Primary treatment of simple cyanide wastes generally takes about 12 hours (depending on the cyanide concentration), and complex cyanides require about 36 hours, or three times longer. CyanoKEM has a proprietary seven-step process for treating complex cyanide wastes.

Treated neutralized slurry from the acid and cyanide primary treatment tanks (A-1 through A-4 and C-1 through C-4) is combined in a 350,000-gal secondary treatment basin that serves as an equalization step for subsequent continuous treatment (Figure 6). The wastewater is pumped from the treatment basin to a 110,000-gal circular clarifier for solids removal, and overflow from the clarifier is pumped to a continuous precipitator/settler unit. The precipitator is the first unit in a series of effluent-polishing steps, where iron sulfide and polymer are added to precipitate and settle any remaining dissolved metals. After the metal precipitation step, the overflow is pumped to two pressure sand filters and then through two carbon columns before being discharged to a POTW. The carbon columns were installed to remove low concentrations of phenols from the effluent.

Backwash water from the two sand filters and the precipitator unit is returned to the secondary treatment basin for equalization and treatment.

Sludge from the primary cyanide treatment tanks is pumped to a sludge-conditioning tank, where lime is added to prepare the sludge for dewatering. The sludge (F006) is pumped from the conditioning tank to a filter press, which produces filter cake (47 to 48 percent solids) at a rate of 20 ft^3 per day. According to CyanoKEM, the sludge contains about 200 ppm total cyanide, which consists primarily of ferri- and ferrocyanides. Effluent from the filter press is returned first to a filtrate tank and then to a primary cyanide treatment tank.

Clarifier underflow is directed to another filter press that generates about 20 yd^3 of filter cake per day, and filtrate is returned to the precipitator tank for additional treatment. Stabilized filter cake from this operation is also shipped to a hazardous waste landfill.

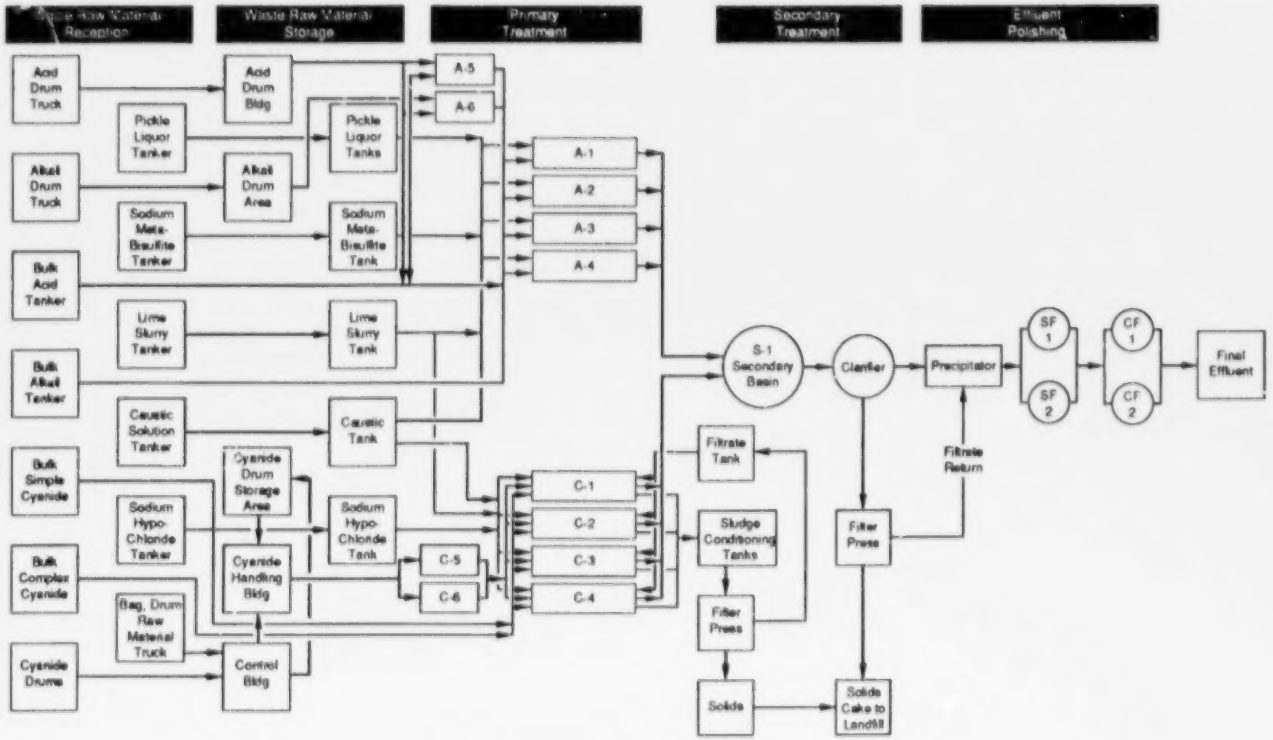

Figure 6. CyanoKEM waste and raw material flow schematic.

WET-AIR OXIDATION

General Description

Wet-air oxidation (WAO) is the liquid-phase oxidation of organics or oxidizable inorganic components at elevated temperatures and pressures. Oxidation is brought about by combining the wastewater with a gaseous source of oxygen (usually air) at temperatures and pressures in the range of about 175° to 327°C (360° to 620°F) and 2069 to 20,690 kPa (300 to 3000 psig), respectively. A feed chemical oxygen demand (COD) concentration of 2 percent is sufficient to cause a temperature rise and to liberate volatile components. The solubility of oxygen in aqueous solutions is enhanced at elevated pressures, and the elevated temperatures provide a strong driving force for oxidation.

Wet-air oxidation has been demonstrated at bench scale, pilot scale, and full scale as a technology capable of breaking down hazardous compounds to carbon dioxide and other less toxic end products (Dietrich 1985). Cyanide in electroplating wastes is converted to carbonate and ammonium ions when oxidized, as shown by the following reaction:

$$2NaCN + O_2 + 4H_2O \rightarrow Na_2CO_3 + (NH_4)_2CO_3 \qquad (4)$$

The major unit operations in the WAO process are wastewater pressurization/air compression, preheat, reaction, cooling, depressurization, and liquid/gas separation. Energy recovery is possible, depending on the temperature of the effluent after the heat exchange with the feed.

There are two forms of continuous reactors: a tower reactor and a cascade of completely stirred tank reactors (CSTR). The tower reactor is a vertical vessel into which air is charged from the atmosphere to interface with the feed. The reactor is sized to allowed 30 minutes to 2 hours retention of the feed (Freeman 1985). The CSTR system consists of a series of horizontal reaction chambers continued within a horizontal cylinder. Air is injected into each reaction chamber as the feed passes from chamber to chamber. Again, the CSTR cascade should be sized to allow 30 minutes to 2 hours reaction.

Off-gasses from WAO systems may have to be treated to reduce the concentration of hydrocarbons. Wet scrubbing, which is commonly used to cool the gas stream, reduces hydrocarbons somewhat. Adsorption columns or thermal oxidation may be required to reduce organic emissions further.

Wastes containing up to 15 percent COD and 6 percent solids can be treated by WAO. For wastes containing less than 2 percent COD, auxiliary fuel must be provided to keep the reaction going (Alliance 1987). High-cyanide-level wastestreams (greater than 1% CN^-) have been successfully treated to below 1 ppm effluent concentration (Sittig 1973). Cyanide destruction of more than 99 percent is typical, and higher cyanide reductions have been reported in some cases. Pretreatment to remove high-density solids (filtration or gravity settling), however, is required for some slurries.

Site Description--Zimpro/Passavant

Zimpro/Passavant is a vendor of waste treatment equipment, including WAO systems; however, no full-scale system is currently in commerical operation for cyanides.

Zimpro now conducts both bench- and pilot-scale WAO feasibility testing on waste streams. The bench-scale testing consists of charging a 0.5-liter-capacity titanium-shaking autoclave with a dilute waste sample and enough air to provide 120 percent of the waste's autoclave oxygen demand (AOD). After charging, the autoclave is placed in a heater shaker mechanism, heated to the desired temperature, and maintained at that temperature for the desired residence time. In the case of the wastes tested in this study, the autoclave oxidations were performed at temperatures of 200°, 240°, and 280°C and a liquid residence time of 60 minutes. The autoclave is then cooled with tap water, and the off-gases are analyzed by gas chromatography for nitrogen, oxygen, carbon dioxide, carbon monoxide, total hydrocarbons (THC), and methane. Each oxidation sample is then filtered and the suspended solids are collected on filter paper. The filtrate and moist solids are then analyzed.

Figure 7 is a flow diagram of the Zimpro pilot-scale system that was used to treat F007 from Amerock. The wastewater or slurry is brought to system pressure by a high-pressure pump. Air from a compressor may be added directly to the waste or to dilution water and preheated to raise the temperature of the mixture at the reactor base so that the exothermic heat of reaction will increase the mixture temperature to the desired maximum. Preheating can be accomplished by an external heat source as shown in Figure 7 or by the reactor effluent. Startup energy is provided by the external heat source to the preheater or an auxiliary heater. The reactor provides adequate residence time for the oxidation reaction the temperature of the wastewater-air mixture rises as the reaction occurs. The reactor effluent is cooled with water (as shown in Figure 7) or with the wastewater-air mixture, usually to about 95° to 135°F. A control valve reduces the pressure of the oxidized liquor/spent air mixture. The gas phase is disengaged from the liquid phase in the separator vessel.

The F007 pilot-scale treatment system at Zimpro/Passavant includes three operations: 1) a blending step to control feed parameters, 2) wet-air-oxidation processing, and 3) treatment of oxidized liquor. Table 6 presents the design parameters and the following subsections discuss the importance of those parameters.

Feed Blending Operation

Upon receipt of four 55-gal drums of F007 waste from Amerock, Inc., Zimpro/Passavant mixed the contents of the waste drums in a water-heated stainless steel tank to ensure a homogenous feed composition. The waste required heating to about 110° to 130°F to maintain its liquid state. Below that temperature range, the waste crystallized because of the high concentration of sodium carbonate, which made handling very difficult. After the waste was thoroughly mixed, the drums were refilled and placed in a hot-water

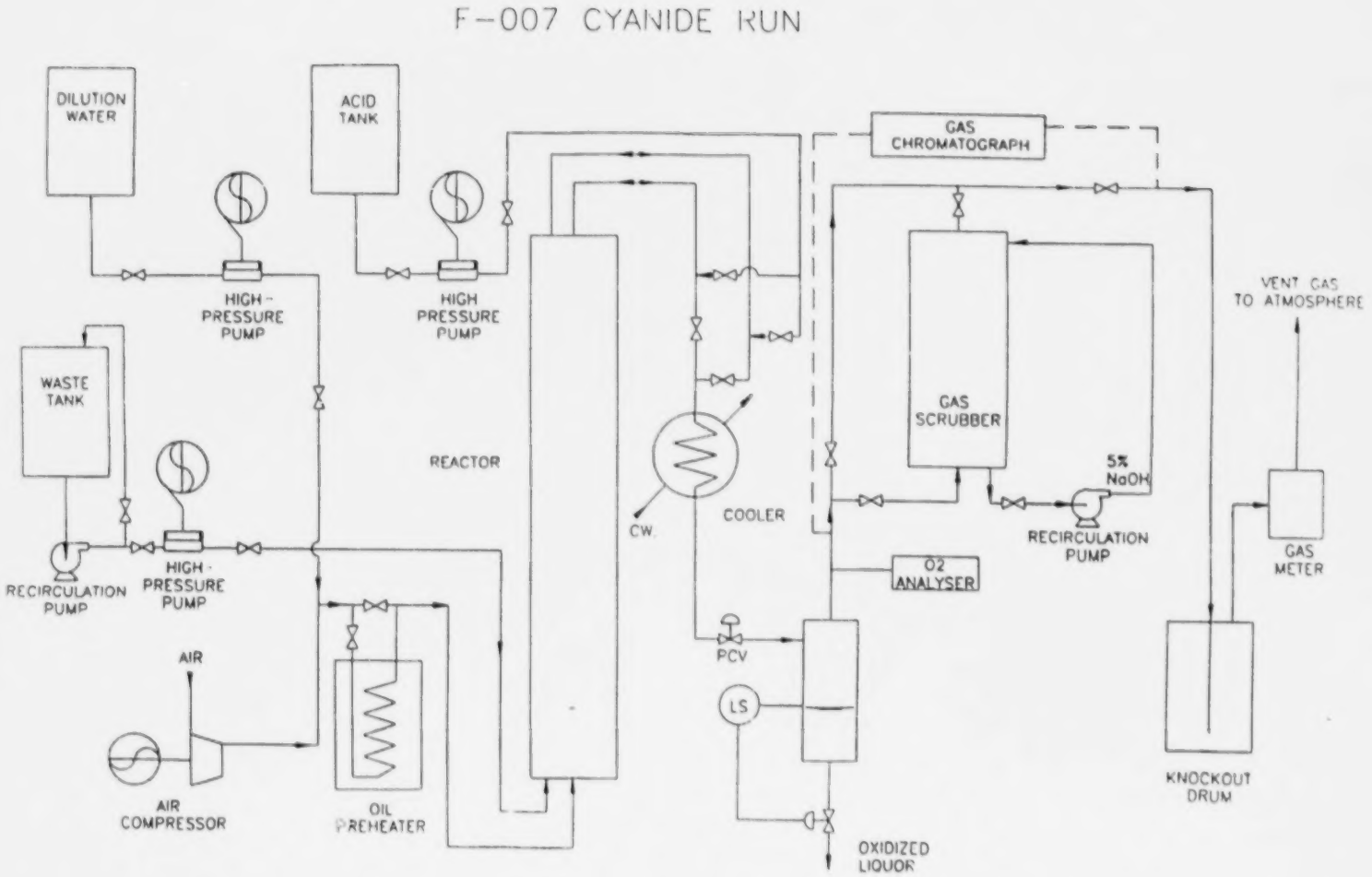

Figure 7. Schematic diagram of Zimpro/Passavant wet-air-oxidation process.

TABLE 6. TYPICAL OPERATING PARAMETERS OF THE WAO PROCESS

Operating parameter	Steady-state condition
Reactor inlet temperature	430° - 470°F
Reactor outlet temperature	440° - 480°F
Reactor pressure	1700 psig
Waste feed rate	2.5 - 3.0 gal/h
Dilution water feed rate	2.5 - 3.0 gal/h
High-pressure air injection rate	60 - 80 scfh
Residual oxygen content of the off-gas	16 - 20%

bath, which was maintained at 110°F. As waste was needed in the performance of the test run, a drum of waste was removed from the water bath, thoroughly agitated with a portable mechanical mixer, and then pumped into the treatment-system feed tank. The feed tank is equipped with a heating coil, a mechanical mixer, and a recycle line to ensure that the feed is maintained at the proper temperature and is homogeneous.

Wet-Air-Oxidation Processing--Amerock test

The steady-state operating conditions of the Zimpro/Passavant WAO process are shown in Table 6. All the parameters listed in Table 6 are key operating parameters; however, the single most important parameter used to determine steady state was the reactor outlet temperature of about 450°F.

Operating phases of the WAO process include warmup (with tap water followed by waste feed), stabilization, steady state, and cool-down (with tap water). The warmup period with tap water typically requires about 4 hours, followed by an additional 2-hour warmup with the waste feed. Waste feed warmup continues until the operating conditions are within approximately 5 percent of the desired conditions, which signals the beginning of the stabilization period. During the stabilization period the operating conditions are continually fine-tuned. Typically, one to three residence times (i.e., about 1 to 3 hours) are required before steady-state is achieved. The steady-state period continues as long as needed to collect all the required samples or until the system falls outside steady state conditions (Table 6). After the test, the system is switched to tap water and cooled down over a period of about 6 to 8 hours.

In the WAO treatment test, dilution water (i.e, tap water) was pumped at a rate of 2.72 gal/h (1745 psig) and combined with 1.1 ft^3/min of compressed air prior to passing through an oil preheater (Figure 7). The preheater heated the tap water/air stream to about 520°F as it entered the base of the

pilot-scale titanium reactor at 1710 psig. The waste feed was pumped approximately 2 feet from the bottom of the 3-in.-i.d., 15-ft-long. reactor at a rate of 2.75 gal/h. Total influent flow rate to the reactor was 4.47 gal/h. Heat tapes spaced evenly along the length of the reactor at 15-in. intervals and the heat of reaction maintained the temperature at about 450°F. The oxidized liquor left the reactor through one of two exit ports. One port was used as the reactor outlet of the oxidized liquor; 18 percent nitric acid was pumped at a rate of 0.55 gal/h (1735 psig) through the other port to remove any carbonate plugging. Every 4 hours throughout the test run, the valves controlling the exit ports were reversed to ensure that the reactor did not plug. From the reactor, the oxidized liquor passed through a tube-in-tube water cooler, which reduced the temperature to about 106°F. The liquor then passed through a pressure control valve that returned the wastewater to atmospheric pressure. The wastewater then entered a gas/liquid separator. The oxidized liquor was collected from the bottom of the separator and the off-gas passed through a caustic scrubber containing a 5 percent NaOH solution. The oxygen content of the off-gas was monitored continuously with an O_2 meter, and a dry-gas meter measured the off-gas flow rate before it was released to the atmosphere. Off-gas samples before and after the scrubber were analyzed for the permanent gases, methane, and total hydrocarbons by a gas chromatograph.

Treatment of Oxidized Liquor

Before discharge of the oxidized liquor to the POTW, the wastewater required neutralization and metals precipitation, which was accomplished by the following process:

1. The oxidized liquor was pumped into a 100-gal holding tank.

2. Nitric acid was added for pH adjustment. Two types of acid were used: 1) spent acid from the reactor acid wash, or 2) concentrated, 38-degree Baume acid.

3. Sufficient acid was added to lower the pH to 8.0 to 8.5. (Care must be taken when the acid is added because a large quantity of carbon dioxide is liberated and the reaction is somewhat violent.)

4. Sulfide in the form of sodium hydrosulfide (NaHS) or sodium sulfide (Na_2S) was added to the tank and mixed.

5. Because the sulfide precipitates are very difficult to filter, diatomaceous earth was added as a filter aid to the slurry to improve filterability.

6. A sample of slurry from the tank was filtered, and a chip of sulfide was added to the filtrate. If the filtrate remained clear, the metal ion precipitation was complete. If a brown precipitate appeared, more sulfide was required. Additional sulfide was added to the holding tank until the filtrate remained clear when a sulfide chip was added.

7. A small plate and frame pressure filter was used for the filtering. The press cloths were precoated with diatomaceous earth before the sulfide solids were filtered to improve filterability and to prevent the sulfide solids from blinding the filter cloth.

Filter cake generated from the treatment of the oxidized liquor was disposed of at a hazardous waste landfill.

ULTRAVIOLET LIGHT/OZONATION

General Description

Ozone is one of the strongest oxidizing agents available. As an oxidant, ozone is strong to break many carbon-carbon bonds and even cleave aromatic ring systems. If ozonation of cyanide is taken to completion, bicarbonate, nitrogen, and oxygen are formed. Complete ozone oxidation of cyanide (via a cyanate intermediate) to end products is as follows (Rice and Browning 1981):

$$CN^- + O_3 \rightleftharpoons CNO^- + O_2 \quad (5)$$

$$2CNO^- + 3O_3 + H_2O \rightleftharpoons 2HCO_3^- + N_2 + 3O_2 \quad (6)$$

Reaction 5 proceeds rapidly and yields the cyanate intermediate (CNO^-). Reaction 6, however, proceeds very slowly, which makes the complete destruction of cyanide to bicarbonate and nitrogen impractical. In general, 2 lb of ozone is required to treat 1 lb of cyanide. Because oxidation by ozone occurs nonselectively, it is generally used only for aqueous wastes that contain a high proportion of oxidizable constituents. Ozonation is believed to be particularly useful as a final treatment step for waste streams that are dilute in oxidizable contaminants but do not meet effluent standards (Alliance Technologies Corp. 1987).

Generally, in the ultraviolet light/ozonation process (UV/O_3), the cyanide stream is mixed with ozone and then enters a reaction chamber in which the stream passes numerous UV lamps. The UV radiation enhances oxidation by direct disassociation of the cyanide radical or through excitation of the various species in the waste stream (Alliance 1987). Complexed cyanides may be more effectively oxidized by ozone in the presence of ultraviolet light (Cushnie 1985). The destruction rate, especially at low cyanide concentrations of a few parts per million, can be enhanced by conducting the treatment at elevated temperatures (approximately 150°F) and/or higher ozone concentration. In industry, the UV/O_3 process is usually equipped with a recycle so that more complete destruction can be achieved. Better cyanide destruction efficiencies can be obtained by using certain metal ions as catalysts (i.e. copper) (Patterson 1985).

Site Description--IITRI

The Illinois Institute of Technology Research Institute (IITRI) in Chicago, Illinois, conducted bench-scale studies of the UV/O_3 system for the treatment of F009 waste. The Master Lock Company in Milwaukee, Wisconsin, was the generator of this waste and provided the necessary quantity of the waste needed to conduct the UV/O_3 testing at IITRI.

ELECTROLYTIC OXIDATION

General Description

Electrolytic oxidation has been used to treat wastes containing high concentrations of cyanide ($\geq$ 1% CN^-) (Sittig 1973). This technology is not suitable for treating rinse waters because of their lower cyanide concentrations.

In this process, the concentrated cyanide waste stream is subjected to electrolysis at temperatures of about 200°F for several days. During this treatment period, the cyanide gradually decomposes to carbon dioxide and ammonia, with cyanate as an intermediate. As the process continues, however, the waste (electrolyte) becomes less capable of conducting electricity and the reaction slows down. Alkaline chlorination may be required to decompose any residual cyanate that may have formed. Electrolytic oxidation has been shown to be less effective on cyanide wastes that contain sulfates (Sittig 1973). Heavy scaling will result at the anode, which will reduce current flow. Wastes containing several tens of thousands of parts per million of cyanide have been treated over 7- to 8-day periods and yielded cyanide levels of less than 0.5 mg per liter (greater than 99.99% destruction) (Sittig 1973).

Site Description--Woodward Governor

The Woodward Governor Company (WGC) of Rockford, Illinois, operates a metal-heat treating facility to case harden carbon and alloy steels. The case hardening process employeed by WGC uses a molten salt bath, typically composed of cyanide and cyanate salts. Residuals from cleanout of the salt-bath pot (F011 waste) are treated by electrolytic oxidation. An F012 wastewater sludge from metal heat treating operations is also generated by WGC. This F012 waste is treated by alkaline chlorination.

In the electrolytic oxidation step, the quantity of solidified cyanide salts (F011) to be treated is placed into the reactor. This reactor, which is heated by internal steam coils, is first partially filled with a lime slurry. The cyanide salt waste is then added by filling a basket with the waste and lowering the basket into the reactor to dissolve the waste. The reactor is then completely filled with tap water and/or lime slurry to its 250-gal capacity and an electrical current is passed through the solution across two sets of electrodes to oxidize cyanide, first to cyanate and then completely to nitrogen or ammonia and carbon dioxide. A typical initial

cyanide concentration in the reactor ranges from 10,000 to 20,000 mg per liter. The cyanide concentration is checked periodically during the course of electrolytic oxidation by a spot test. The single spot test used by plant personnel consists of precipitate formation and color change upon addition of a drop of chloramine-T and a barbituric acid solution to a specified amount of waste. Operators typically allow at least 1 hour of treatment time for each 5 lb of cyanide waste added to the electrolytic oxidation reactor at the start of treatment.

After electrolytic oxidation, the waste is fed into a steam-heated batch reactor, where chemical oxidation occurs over a 1- to 2-hour period by reaction of the cyanide with sodium hypochlorite. This chlorination treatment step further reduces the cyanide concentration. A second-stage alkaline chlorination is conducted to convert cyanate to carbon dioxide and nitrogen. (See Figure 8 for a schematic diagram of the F011 Treatment Operation.)

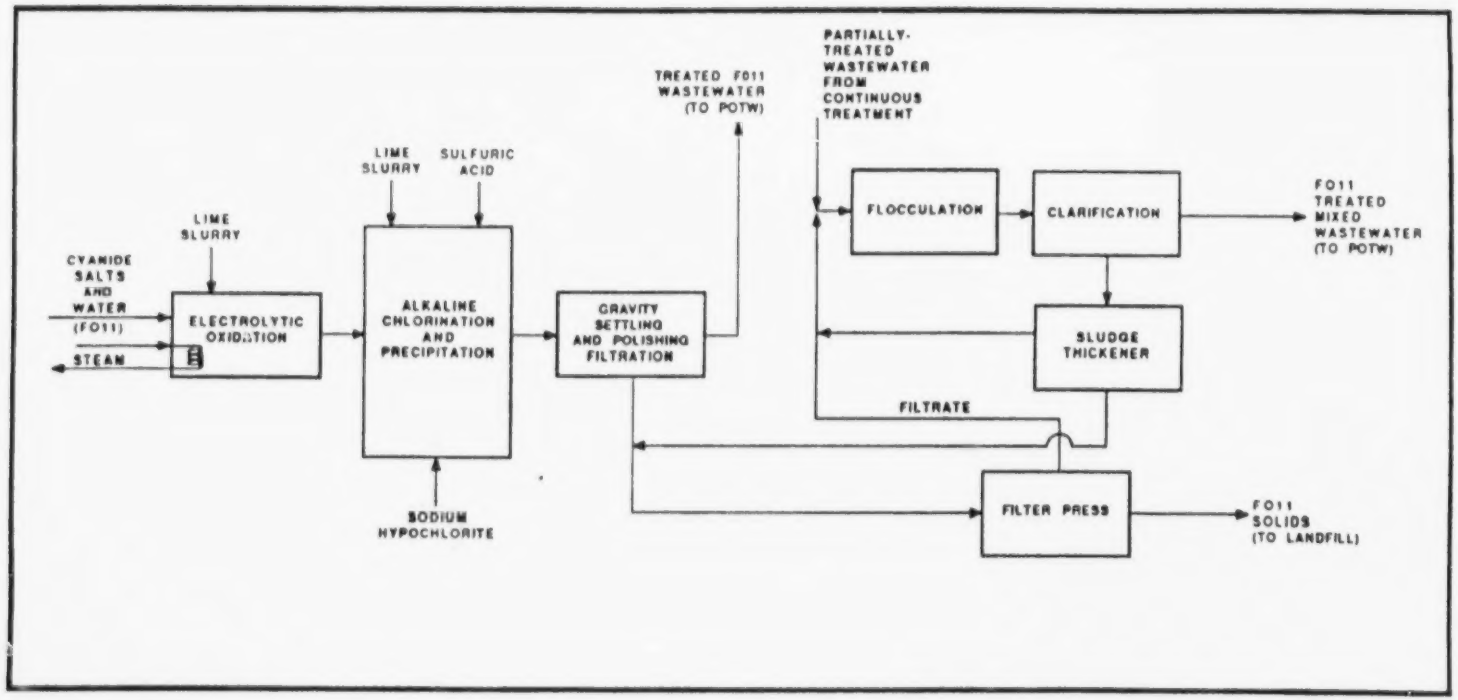

Figure 8. Schematic diagram of the batch F011 cyanide treatment process at Woodward Governor, Rockford, Illinois.

SECTION 4

CHEMICAL PRECIPITATION

Chemical precipitation is the most common treatment method used by the electroplating industry for removal of metals from wastewaters. Sludges generated by this technique are typically solidified/stabilized for disposal. This section presents a general process description of the chemical precipitation used by the individual sites in this study. It also describes the site of the John Deere and company facility.

PROCESS DESCRIPTION

Precipitation of metal-laden wastewaters involves the addition of chemicals to alter the physical state of the dissolved or suspended metals and to facilitate their removal through sedimentation. Chemicals used to precipitate metals for aqueous streams include caustic soda, lime, sodium sulfide, ferrous sulfide, soda ash, and sodium borohydride. Complexed metal wastewaters cannot be effectively treated by such chemical additions; therefore, the use of reducing agents is needed before their removal from the water matrix by precipitation. The reduction process involves the transfer of electrons to the chemical being reduced (reductant) from the chemical initiating the transfer (the reducing agent). Four commonly used reducing agents are sulfur dioxide, ferrous sulfate, sodium borohydride, and sodium bisulfite. For collodial suspensions, characterized by their balance of attractive and repulsive forces, the use of coagulants/flocculants is required for adequate precipitation. Coagulants/flocculants destabilize the suspension by reducing the repulsive forces so the particles can agglomerate. Examples of coagulants/flocculants include lime, alum, and synthetic polyelectrolytes.

Precipitation, reduction, and coagulation/flocculation are followed by sedimentation (settling). Typical settling times for heavy metal particles are between 90 and 150 minutes, depending on the waste being treated (Metcalf & Eddy 1979). Precipitation can occur in both batch or continuous sedimentation systems. With continuous systems, sedimentation tankage (clarifiers) should be sized to accommodate a wastewater flow of 0.5 gal/min per square foot of clarifier surface area (Metcalf & Eddy 1979). After settling has occurred, a sludge layer (which typically contains about 1 to 2 percent solids) forms at the bottom of the tank. This sludge is then sent to additional tanks (sludge thickeners), which provide subsequent settling to approximately 5 to 10 percent solids. The resultant sludge is then sent through pressure or vacuum filtration to increase the sludge solids content to about 15 to 50 percent, depending on the type and amount of chemical

additives used. The sludge cake is then shipped for treatment and disposal at a hazardous waste landfill. Figure 9 is a flow diagram of a typical continuous precipitation treatment system. The reduction step is only required for certain applications.

Specific precipitation processes, including the use of reducing agents and coagulation aids, are discussed in the following subsections.

Hydroxide Precipitation

For many heavy metals, precipitation is accomplished by adjusting the pH of the wastewater to alkaline, which causes the soluble metal ions to form insoluble metal hydroxides. This pH adjustment is usually achieved by the addition of caustic (sodium hydroxide) or lime (calcium hydroxide). For metal hydroxide species, the solubilities are known to increase with both rising and falling pH values outside the pH 7 to 10 range. Table 7 presents the pH ranges typically used to precipitate a metal hydroxide and the approximate effluent discharge after sedimentation (in a well-run treatment system). Because the discharge must be in the proper pH range (pH of 6 to 9) and because of the differences in industrial waste compositions, actual industrial effluent concentrations from precipitation systems tend to be greater than their minimal solubilities. Sand filtration of the effluent after sedimentation can further reduce the metal concentrations in the discharge (Patterson 1985). Coprecipitation with other metals can enhance the removal of a given metal species.

TABLE 7. TYPICAL WASTEWATER DISCHARGE CONCENTRATIONS FROM METAL HYDROXIDE PRECIPITATION PROCESSES[a]

Metal hydroxide	pH range for treatment	Typical effluent discharge after sedimentation, mg/liter
Aluminum	6-7	0.10
Cadmium	>10	0.5
Chromium (III)	7-8	0.10
Copper	9-10	0.50
Nickel	10-11	>1.0
Zinc	8-11.5	>1.0
Lead	9.5-10.5	>1.0
Silver	10.5-11.5	0.50

[a]Source: Alliance Technologies Corporation (1987).

Sulfide Precipitation

Chelated wastewaters (e.g., those containing EDTA) can severely hinder the metals removal of precipitation systems. Sulfide precipitation, however, which drops out metal ions as very insoluble sulfides, has been shown to yield high metal removals even in highly chelated wastewater (Cushnie 1985). This process is used as an alternative to hydroxide precipitation or as a polishing step after hydroxide precipitation. Two different processes are

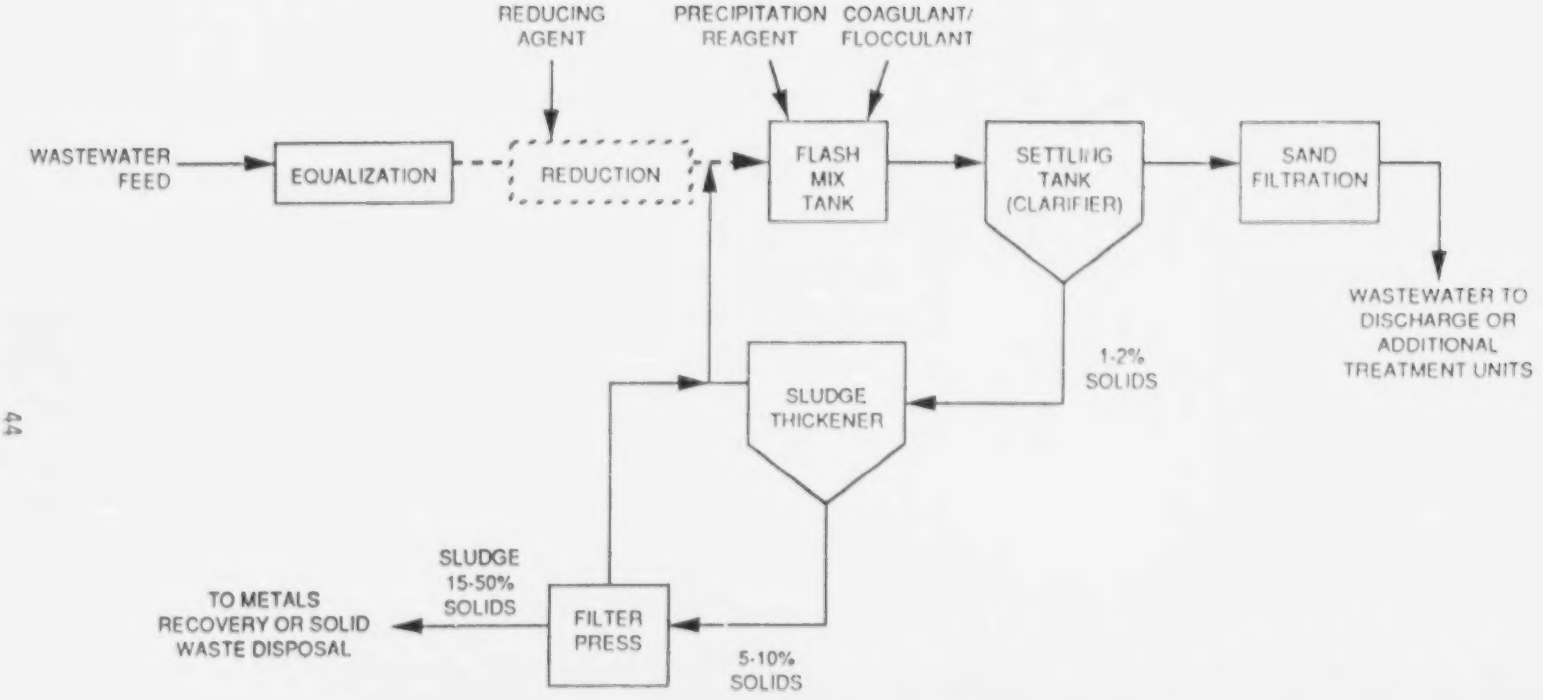

Figure 9. Flow diagram of a typical continuous precipitation system.

used for sulfide precipitation--the soluble sulfide process and the insoluble sulfide process. The soluble sulfide process uses sodium sulfide as the treatment reagent, whereas the insoluble sulfide process uses ferrous sulfide. Both processes generate metal sulfide sludges that tend to be more difficult to dispose of properly because of potential sulfide reactivity (Cushnie 1985). The insoluble sulfide process generates a larger volume of sludge than does hydroxide precipitation because of the liberation of ferrous ions during treatment and the subsequent conversions of these ions to ferrous hydroxide (Cushnie 1985). Removal levels for arsenic, cadmium, lead, mercury, nickel, silver, and zinc are significantly better with sulfide precipitation than with hydroxide precipitation because their sulfide solubilities are lower than their corresponding hydroxide solubilities.

For effective metals removal, the pH of the waste water must be maintained within the neutral to slightly alkaline range. Contact with acidic wastewaters will result in poorer removal and can cause the emission of hydrogen sulfide (H_2S) gas (Cushnie 1985).

Phosphate Precipitation

Pilot studies have been conducted to evaluate phosphate precipitation as a treatment alternative for recovering chromium from mixed metal solutions (Twidwell 1987). Phosphate, in the form of phosphoric acid H_3PO_4, can effectively strip trivalent cations from solution in preference to divalent cations under low pH conditions. Phosphate products filter easily and can be compacted to a high solids content. Results of work conducted on metal sludge leachates have shown greater than 99 percent removals of chromium at pH 3.5 using phosphate (Twidwell 1987).

Chromium Reduction

Ferrous sulfate ($FeSO_4$) is industry's reagent of choice for chromium reduction because of its abundance and low cost. With the use of $FeSO_4$, the pH of the chromate waste stream must be between 2 and 3 for rapid reduction, as shown in the following:

$$3Fe^{+2} + HCrO_4^- + 7H^+ \rightarrow 3Fe^{+3} + 4H_2O + Cr^{+3} \quad (7)$$

Subsequent neutralization results in large volumes of iron hydroxide sludges, which makes disposal costly. An alkaline ferrous sulfate reduction process is currently being studied. This process requires that the pH be maintained between 7 and 10; therefore, it can take place in the neutralization/precipitation tankage (Cushnie 1985). One deficiency of this alkaline process is the difficulty encountered in accurately controlling ferrous sulfate additions to the wastewater. Sulfur dioxide, sodium bisulfate, and metabisulfate are other reagents used for reduction of chromium.

Coagulation/Coprecipitation (Alum, Lime, and Polyelectrolytes)

Coagulation/flocculation systems improve sedimentation of precipitated metal particles. The rate at which coagulated particles coalesce is related

primarily to the frequency of the collisions between the particles. Collisions occur as a result of the heavier faster particles overtaking the lighter slower particles. As a result, the frequency of collisions is proportional to the particle concentration and the difference in settling velocity. Because the number of collisions typically increase with time, the degree of flocculation usually increases with the residence time (EPA 1987). Other factors that affect the agglomeration of particles include the nature of the surface, the presence of electrical charges, the shape, and the density. Inorganic coagulants are used primarily for waste streams having dilute concentrations of insoluble constituents. These coagulants, however, add to the overall sludge generation. Lime, alum, and ferric chloride are the inorganic coagulants of choice by industry. Synthetic polyelectroytes are used mainly with heavy metal precipitates. These chemicals use chemical bridging and physical entrapment to coalesce the precipitated metals. Anionic polymers are generally used because heavy metal precipitates tend to carry slightly positive charges. A natural anionic polymer, ISX, has also been developed as a coagulant. Because of handling difficulties and disposal problems, however, the natural anionic polymer has not been as widely accepted as have the synthetic polyelectroytes and inorganic coagulants.

Coprecipitation is the process of precipitating a given metal species in association with other metal species. For some metal ionic forms, such as arsenate (AsO_4^{-3}), coprecipitation is the treatment method of choice. Coprecipitation involves both absorption of the soluble ion onto a bulk solid and coagulation of fine solids by the bulk precipitate.

SITE DESCRIPTION--JOHN DEERE AND COMPANY

John Deere's Waterloo, Iowa, operations include four major facilities: John Deere Engine Works, John Deere Tractor Works, John Deere Components Works, and John Deere Product Engineering Center. These facilities generate a variety of wastes that are treated on site in the wastewater treatment plant. The wastes include electroplating sludges, spent electroplating baths, painting wastes, caustic paint-stripping wastes, kolene sludge from castings cleaning, spent pickling acids, aluminum conditioner, caustic cleaners, waste oils, and miscellaneous acids and alkaline wastes. The wastewater treatment plant receives about 300 gal of copper cyanide sludge (F008, 1 to 2% CN) twice a year, 500 gal of spent copper cyanide plating bath solution (F007, 1 to 2% CN) once a year, and a total of 75,000 gal of cyanide rinse waters per year (100 ppm CN). The treatment plant does not receive any F009. This report focuses on the wastewater treatment units involved in the phosphoric acid metal precipitation process and alkaline chlorination.

John Deere operates both a batch and continuous phosphoric acid metal precipitation process (Figure 10). Cyanide treatment occurs only in the batch mode. In the batch process, which takes about 4 hours per batch, wastewater is pumped to a 16,000-gal equalization tank (T-41) followed by a 9000-gal reactor tank (T-45). Depending on the type of wastewater and the level of treatment desired, the reactor tank is equipped with chemical feed

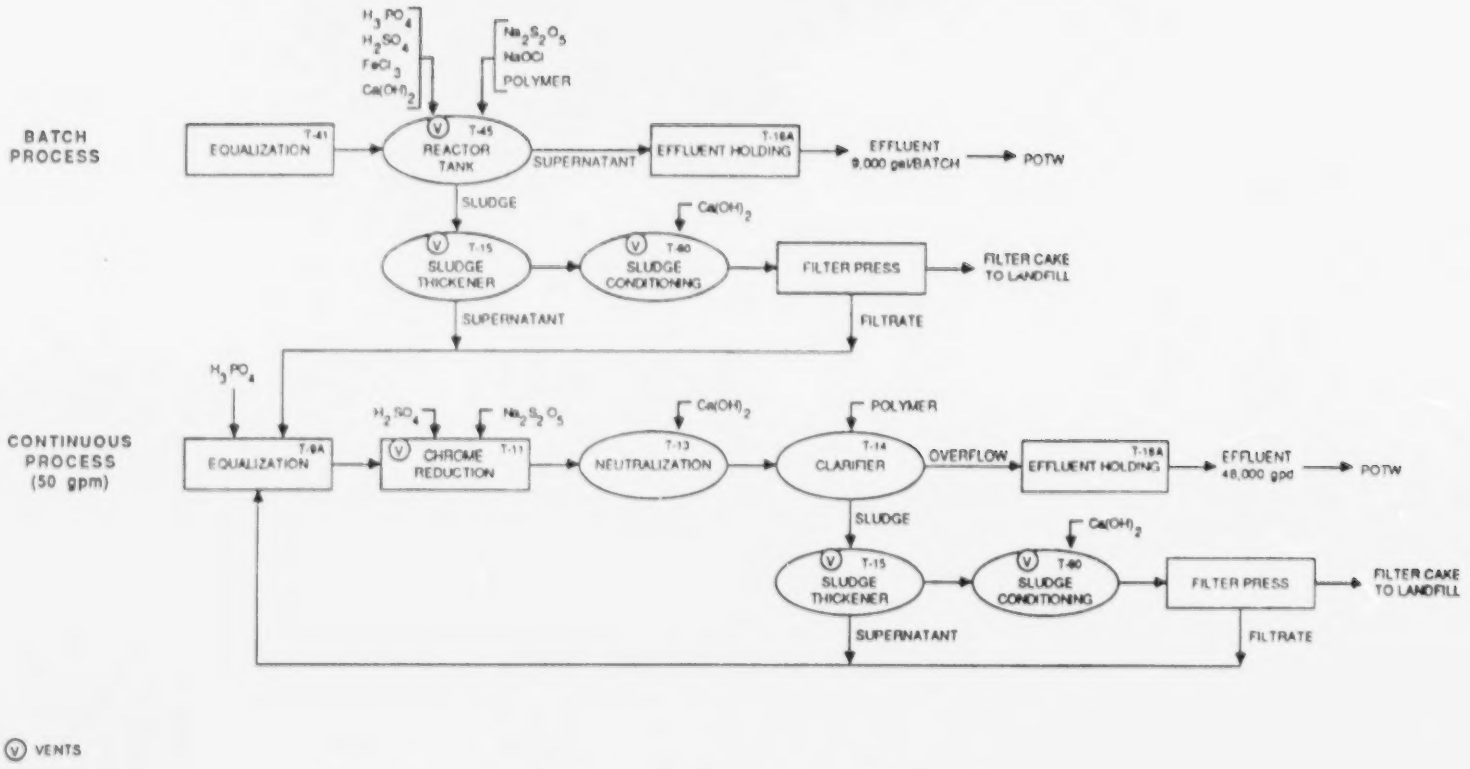

Figure 10. Phosphoric acid metal precipitation at John Deere.

lines for the addition of phosphoric acid, sulfuric acid, ferric chloride, lime, sodium disulfite, sodium hypochlorite, and polymer. The reactor tank serves as a flash mix tank, a flocculation tank, and a sedimentation tank. The reactor tank is also equipped with pH meters and oxidation-reduction potentiometers (ORPs) for use on one- and two-stage alkaline chlorination during the treatment of cyanide-bearing waste streams. Supernatant from the reactor tank is pumped to a 40,000-gal holding tank prior to discharge to the POTW. Sludge from the reactor tank is pumped to a 7500-gal sludge thickener (T-15). The thickened sludge is pumped to a 5500-gal conditioning tank (T-60), where 12 to 13 percent lime is added to prepare the sludge for dewatering in the filter press. The Netzsch filter press generates about 65 ft^3 of filter cake per batch, which takes about 1.5 hours. John Deere runs about two batches a day. The filtercake (50 to 60 percent solids) is disposed of at a hazardous waste landfill. Supernatant from T-15 and filtrate from the filter press are pumped to the equalization tank (T-9A) in the continuous treatment process.

SECTION 5

STABILIZATION/SOLIDIFICATION OF METAL-FINISHING WASTES

Stabilization/solidification involves the mixing of a hazardous waste with a binder material for enhancement of the physical and chemical properties of the waste and the chemical binding of any free liquid (EPA 1986). The binder is typically a cement, pozzolan, or thermoplastic. Stabilization involves a chemical reaction that converts inorganic waste material to its least soluble and most environmentally inert form. Solidification systems improve the handling and physical characteristics of the waste and decrease the surface area from which volatilization, leaching, or spillage losses can occur. A solidified waste is encapsulated in a monolithic solid of high structural integrity. The encapsulation may be of fine waste particles (microencapsulation) or a large block or container of wastes (macroencapsulation). The two terms stabilization and solidification are commonly used together because they are both instrumental in immobilizing hazardous constituents in the waste.

BACKGROUND

The U.S. Army Corps of Engineers Waterways Experiment Station (WES) in Vicksburg, Mississippi, conducted stabilization/solidification testing on selected metal-finishing hazardous wastes under an interagency agreement with the EPA. Following stabilization/solidification of the metal-finishing wastes, WES performed the toxicity characteristic leaching procedure (TCLP) on the untreated and treated material and forwarded the extracts to an independent laboratory for chemical analysis. The TCLP extracts processed by WES represented EPA Hazardous Waste Nos. F006, F011, F012. Hazardous Waste F006 is described as wastewater treatment sludges from electroplating operations, F011 is described as spent cyanide solutions from salt-bath-pot cleaning in metal heat-treating operations, and F012 is described as quenching wastewater treatment sludges from metal heat-treating operations where cyanides are used in the process. The WES stabilized/solidified three F006 waste streams from John Deere in Waterloo, Iowa; Amerock in Rockford, Illinois; and Master Lock in Milwaukee, Wisconsin. The F011 and F012 wastes were both collected at Woodward Governor in Rockford, Illinois.

DESCRIPTION OF THE WES STABILIZATION/SOLIDIFICATION PROCESS

Three different pozzolan binders (lime/fly ash, portland cement, and kiln dust) were tested by WES to determine their potential application to metal-finishing waste codes. Lime/fly ash and kiln dust pozzolanic processes

use a finely divided, noncrystalline silica in the fly ash and calcium in the lime to produce low-strength cementation. Waste containment is obtained by entrapping the waste in the pozzolan concrete mix (microencapsulation). Pozzolan-portland cement systems produce a type of waste/concrete composite. Microencapsulation of the contaminants in the concrete matrix provides containment. The addition of soluble silicates to the mix helps to accelerate hardening.

The stabilization/solidification process involves the addition of water and binder material to the waste, followed by mixing and a curing period. The waste-binder mix samples are cured at room temperature for over 48 hours. The samples are placed in a curing box under specific temperature and humidity conditions. The samples are then removed from the curing box to a cool place. The cooled concrete test cubes are subjected to a compressive strength test to evaluate the technical and economical feasibility of the binders, or are subjected to a leaching performance evaluation [toxicity characteristic leaching procedure (TCLP) and waste extraction test (WET)]. Figure 11 is a flow diagram of the stabilization/solidification process used at WES (U.S. Army 1988).

An initial screening test is used by WES to determine the appropriate water-to-binder/waste ratio for each of the binders used and to narrow the range of binder-to-waste ratios used in the more detailed evaluation. The optimal water-to-binder/waste ratio is determined by a Cone Index (CI) Test on test samples after 48-hour curing at room temperature. The CI value is reported as the force per unit surface area of a cone base required to push the cone through the test sample at a rate of 72 in./min. Once these ratios are determined by the CI, new specimens are created for detailed unconfined compressive strength (UCS) testing to be conducted on cubes cured 7, 14, 21, and 28 days. The UCS test subjects each test cube to crushing with a compression apparatus to define and characterize the effects of the stabilization/solidification process on the physical characteristics of the waste. The UCS is reported as the force required to fracture the test cube. A conservative pass/fail criterion of 50 pounds per square inch (psi) was used to select samples for chemical analysis.

Leaching performance is the primary criterion in all treatability work, and is therefore the most relevant of parameters. WES performed the TCLP and WET tests on samples cured for 24 hours and 28 days. The TCLP was developed to determine which trial mix leached the least on a unit basis.

The test cubes were subjected to TCLP extractions in accordance with Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846, 3rd ed., 1986. The WET testing was performed in accordance with State of California regulations (California Administrative Code, Title 22).

Section 6 includes a detailed discussion of the results of the stabilization/solidification tests conducted on EPA Hazardous Wastes F006, F011, and F012.

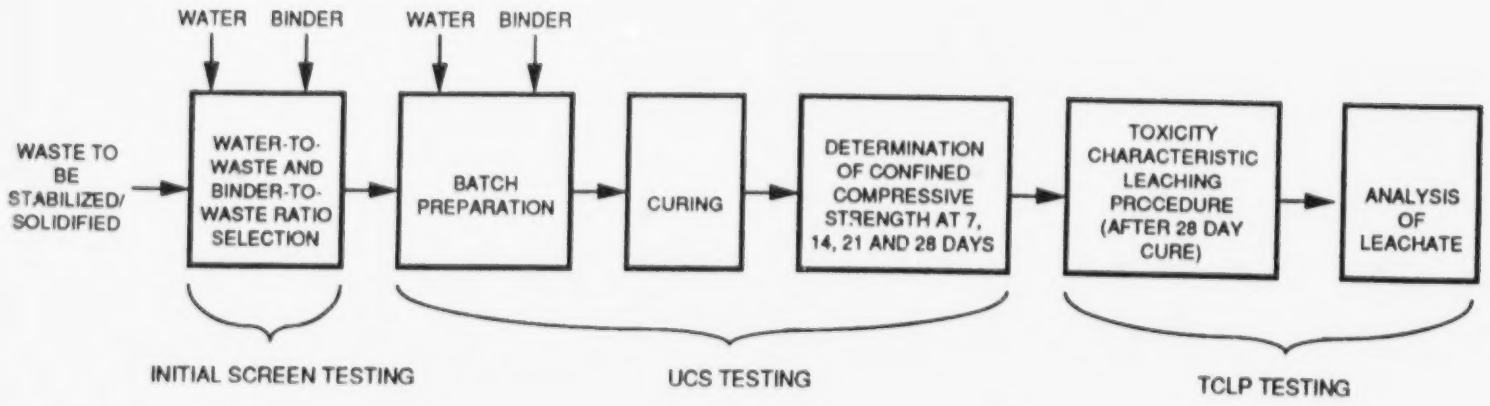

Figure 11. Flowchart for WES stabilization/solidification processing.

SECTION 6

RESULTS AND CONCLUSIONS

WASTE CHARACTERIZATION

The following subsections summarize the results of the sampling of metal-finishing sites for RCRA-listed F006 filter cakes, F007 and F009 wastewaters, and F019 filter cakes to obtain information on specific waste characteristics.

F006 Filter Cake

Amerock--

A total of six raw F006 filter cake samples were collected by PEI at Amerock Corporation, Rockford, Illinois, on September 1, 1988. Three 8-oz glass jars of the filter cake were obtained for analysis by PEI's laboratory in Cincinnati, Ohio. Three additional 6-gallon buckets of the filter cake were collected to send to the U.S. Army Corps of Engineers' WES in Vicksburg, Mississippi, for stabilization/solidification testing if the waste proved to contain appreciable levels of complexed cyanide. Testing details were presented in Section 4 of this report.

The 8-oz filter cake samples were analyzed for BDAT metals, total compositional cyanide (total and amenable), and TCLP cyanide (total and amenable). A list of specified analytes is provided in Table 8. Matrix spikes and matrix spike duplicates (for all constituents) were performed on one sample of the filter cake. Data obtained in the analysis of the filter cake are confidential; however, some key analytical points should be discussed. Analysis of the TCLP residue revealed that more than half (56%) of the total cyanide in raw waste remained in the residue and did not leach. Cyanide spike recoveries were found to satisfy OSWER QA objectives of greater than 20 percent. Metal spike recoveries satisfied OSWER QA objectives of greater than 20 percent except for silver, for which spike recoveries were about 10 percent. Because silver is a noncritical parameter, no repeat analysis was taken.

Master Lock--

On October 18, 1988, PEI collected raw F006 filter cake samples at the Master Lock Company, Milwaukee, Wisconsin, for chemical analysis and stabilization/solidification testing. Master Lock indicated that the conventional wastewater treatment sludge (as opposed to the treatment of complexed and batch wastewaters) had the highest cyanide and metal concentrations. Therefore, PEI collected a total of six samples of conventional treatment filter

cake. Two 8-oz clear glass jars were required for each of the six samples. PEI also collected three 6-gallon plastic buckets of the waste filter cake for WES stabilization/solidification testing. It was noted that some of the waste placed in the buckets may have come from the complexed or batch waste streams. PEI's laboratory in Cincinnati, Ohio, performed all the chemical analysis.

TABLE 8. LIST OF AMEROCK F006 ANALYTES

BDAT metals	
154 Antimony	161 Lead
155 Arsenic	162 Mercury
156 Barium	163 Nickel
157 Beryllium	164 Selenium
158 Cadmium	165 Silver
159 Chromium (total)	156 Thallium
221 Chromium (hexavalent)	167 Vanadium
160 Copper	168 Zinc
Inorganic nonmetallics	**TCLP**
169 Cyanide (total)	169 Cyanide (total)
169 Cyanide (amenable)	169 Cyanide (amenable)

The filter cake samples were analyzed for BDAT metals and total compositional cyanide. The TCLP leachate and residue were analyzed for cyanide (total, amenable, and WAD). Table 9 lists the specific analytes. Matrix spikes and matrix spike duplicates for all constituents were performed on one of the samples.

TABLE 9. LIST OF MASTER LOCK F006 ANALYTES

BDAT metals	
154 Antimony	161 Lead
155 Arsenic	162 Mercury
156 Barium	163 Nickel
157 Beryllium	164 Selenium
158 Cadmium	165 Silver
159 Chromium (total)	166 Thallium
221 Chromium (hexavalent)	167 Vanadium
160 Copper	168 Zinc
Inorganic nonmetallics	**TCLP**
169 Cyanide (total)	169 Cyanide (total)
169 Cyanide (amenable)	169 Cyanide (amenable)
169 Cyanide (WAD)	169 Cyanide (WAD)

Tables 10 and 11 present the analytical data obtained from the Master Lock F006 filter cake.

Total cyanide concentrations in the raw waste averaged 2392 µg/g, and total cyanide detected in the TCLP leachate of the raw waste averaged less than 0.04 mg/liter (or 0.8 µg/g), which is slightly above the method detection limit of 0.02 mg/liter or 0.5 µg/g. Analysis of the TCLP residue showed that about half (49%) of the total cyanide in tne raw waste remained in the residue and did not leach. Amenable cyanide in the raw and TCLP residue samples could not be determined; however, EPA Method 9010 did appear to work on the TCLP leachate. The concentration in the leachate ranged from undetected to 0.16 mg/liter.

The WAD cyanide was determined on the Master Lock samples in an effort to quantify the amenable cyanide fraction of the total cyanide in the raw waste. In the raw waste, WAD cyanide accounted for about 5 percent of the total cyanide, whereas it represented about 15 percent of the total cyanide in the TCLP residue. Negligible concentrations of WAD cyanide were found in the TCLP leachate. Analytical discrepancies, however, make the significance of these data questionable.

Metal analyses of the Master Lock F006 samples indicate elevated concentrations of cadmium, nickel, copper, chromium, and zinc. Cadmium concentrations averaged 39,867 µg/g, nickel averaged 11,650 µg/g, copper averaged 7928 µg/g, chromium averaged 4820 µg/g, and zinc averaged 4682 µg/g. Silver was the only constituent that did not satisfy the OSWER QA objective of greater than 20 percent for spike recoveries. Again, because silver is not a critical parameter, no repeat analysis was taken.

John Deere and Company--

On May 21, 1987, PEI collected raw F006 filter cake samples at John Deere and Company, Waterloo, Iowa, for characterization analysis and stabilization/solidification testing. A sample of electroplating wastewater from T-9A (influent to the continuous phosphoric acid metal precipitation process) was collected, along with a sample of F006 filter cake from the dewatering of the precipitated sludge. About 15 gallons of the filter cake was also collected for stabilization/solidification testing at WES.

The influent wastewater was analyzed for Appendix IX volatile and semivolatile organics, Appendix IX metals, sulfide, fluoride, ammonia, purgeable organic carbons (POCs), and nonpurgeable organic carbons (NPOCs). The filter cake was analyzed for Appendix IX volatile organics, Appendix IX metals, sulfide, fluoride, ammonia, POC, NPOC, TCLP volatile organics, and TCLP metals. PEI's laboratory in Cincinnati, Ohio, performed all the chemical analyses.

Tables 12 and 13 present the results of the analyses of John Deere's F006 waste. Metal analyses of the samples indicate elevated concentrations of chromium (1650 mg/liter). Ammonia levels were also high (6850 µg/g). Analysis of the TCLP extract for metals showed only arsenic to be above detection limits. The value for arsenic, however, was three orders of magnitude below the regulatory limit.

TABLE 10. SUMMARY OF MASTER LOCK F006 CYANIDE ANALYSES[a,b]

Sample No.	Raw samples, µg/g			TCLP leachate, m/L (µg/g)			TCLP residue, µg/g			Percent recovered	
	CN(T)	CN(A)	CN(WAD)	CN(T)	CN(A)	CN(WAD)	CN(T)	CN(A)	CN(WAD)	CN(T)	CN(WAD)
MLOCK-CK-1	7080	NA	89	0.16(3.2)	0.16(3.2)	<0.02(<0.4)	94	NA	454	4	510
MLOCK-CK-2	2280	NA	130	0.03(0.6)	0.03(0.6)	<0.02(<0.4)	1390	NA	224	61	172
MLOCK-CK-3	2560 (94.0%/0%)[d] (68.0%/0%)[d]	NA	78 (266%/0%)[d] (101%/102%)[d]	<0.02(<0.4)[d] (149%/179%)[d]	<0.02(<0.4)	13.7(274) (97.7%/174%)[d]	860 (14.8%/0%)[d]	NA	111 (92.4%/85.6%)[d]	34	142
MLOCK-CK-4	2860	NA	174	0.02(0.4)	0.02(0.4)	<0.02(<0.4)	1420	NA	205	50	118
MLOCK-CK-5	1800	NA	195	<0.02(<0.4)	<0.02(<0.4)	<0.02(<0.4)	678	NA	53	38	27
MLOCK-CK-6	2770	NA	53	<0.02(<0.4)	<0.02(<0.4)	<0.02(<0.4)	1720	NA	84	62	158
Range	1800-2860	-	53-195	<0.02-0.16 (<0.4-3.2)	<0.02-0.16 (<0.4-3.2)	<0.02-13.7 (<0.4-274)	1390-1720[e]	-	53-454	34-62[e]	27-510
Average	2392	-	120	<0.04(<0.8)	<0.04(<0.8)	<2.3(46)	1214[e]	-	188	49[e]	188

[a] Total cyanide and weak acid dissociable cyanide method detection limits are 2 µg/g for raw waste, 0.02 mg/L for TCLP leachate, and 5 µg/g for TCLP residue. Amenable cyanide method detection limits are 0.02 mg/L for TCLP leachate.

[b] Extraction fluid No. 2 (pH = 2.88 ± 0.05) was used in TCLP procedure.

[c] NA = Not analyzable by EPA Method 9010. Cyanide concentrations after alkaline chlorination were higher than the total cyanide concentrations, which results in a negative amenable cyanide concentration. This is caused by sample interference. Therefore, amenable cyanide data cannot be reported. ence. Therefore, amenable cyanide data cannot be reported.

[d] Spike recovery for matrix spike/matrix spike duplicate in percent.

[e] Sample MLOCK-CK-1 was not used in these calculations because data appear to be significantly inconsistent with the other data points.

TABLE 11. SUMMARY OF MASTER LOCK F006 METAL ANALYSES

Constituent	Sample Number						Range	Average	MS, MLOCK-CK-3, % recovered	MSD, MLOCK-CK-3, % recovered
	MLOCK-CK-1, µg/g	MLOCK-CK-2, µg/g	MLOCK-CK-3, µg/g	MLOCK-CK-4, µg/g	MLOCK-CK-5, µg/g	MLOCK-CK-6, µg/g				
Antimony	<6.14	<5.90	<6.02	<6.20	<6.20	<6.02	<5.90 - <6.20	<6.08	78.3	72.3
Arsenic	0.76	0.67	0.49	0.48	0.58	0.71	0.48 - 0.76	0.62	78.1	75.5
Barium	7.92	6.44	7.00	6.39	6.67	6.99	6.39 - 7.92	6.90	71.3	74.2
Beryllium	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	72.4	72.1
Cadmium	41500	41000	38700	35500	39600	42900	35,500 - 42,900	39,867	167	206
Chromium, total	4980	4850	4620	4290	4920	5380	4,290 - 5,380	4,840	130	167
Chromium, VI[a]										
Copper	8030	8020	7650	7100	8070	8700	7,100 - 8,700	7,928	99.3	107
Lead	<7.46	<7.46	9.70	<7.39	<7.53	<6.92	<6.92 - 9.70	<7.74	74.8	75.8
Mercury	<0.132	<0.130	<0.131	<0.126	<0.133	<0.137	<0.126 - <0.137	<0.132	98.6[b]	
Nickel	12500	11900	11300	10300	11500	12400	10,300 - 12,500	11,650	112	127
Selenium	<0.16	<0.16	<0.16	<0.16	<0.16	<0.15	<0.15 - <0.16	<0.16	72.3	67.5
Silver	<0.85	<0.85	<0.85	<0.84	<0.86	<0.79	<0.79 - <0.86	<0.84	7.5	4.4
Thallium	<12.6	<12.6	<12.6	<12.5	<12.7	<11.7	<11.7 - <12.7	<12.4	74.6	72.0
Vanadium	4.05	4.44	3.75	3.76	3.66	4.07	3.66 - 4.44	3.96	72.9	73.9
Zinc	4750	4650	4560	4160	4650	5320	4,160 - 5,320	4,682	102	105

[a] EPA Method 7196 (colorimetric method) did not work on these samples because of a possible matrix interference.

[b] MS/MSD for mercury performed on MLOCK-CK-1.

TABLE 12. ANALYSIS OF JOHN DEERE F006 FILTER CAKE

Constituent	Concentration, µg/g
Fluoride	268
Sulfide	21
Ammonia	6,850
NPOC	16
POC	305
Aluminum	270
Antimony	22.4
Arsenic	<0.4
Barium	28.8
Beryllium	<0.1
Cadmium	0.37
Calcium	88,200
Chromium	1,650
Cobalt	<2
Copper	135
Iron	5,930
Lead	184
Magnesium	998
Manganese	79.1
Mercury	<0.2
Nickel	11.8
Osmium	29.7
Potassium	52.2
Selenium	<0.03
Silver	<0.6
Sodium	384
Thallium	<20
Tin	35.6
Vanadium	1.26
Zinc	2,510

TABLE 13. ANALYSIS OF JOHN DEERE F006 TCLP EXTRACT FOR METALS (mg/liter)

Metal	Regulatory limit	Results
Arsenic	5.0	0.004
Barium	100.0	<0.002
Cadmium	1.0	<0.003
Chromium	5.0	<0.02
Lead	5.0	<0.083
Mercury	0.2	<0.0003
Selenium	1.0	<0.003
Silver	5.0	<0.006

F009 Wastewater--Master Lock Company

On March 16, 1989, PEI collected an alkaline chlorinated effluent (F009) sample at the Master Lock Company, Milwaukee, Wisconsin. Three 30-gal polyethylene drums were filled with this wastewater for testing purposes. IT Analytical Services in Pittsburgh, Pennsylvania, performed all of the chemical analyses. Table 14 presents the analytical data for the F009 wastewater. The total cyanide level in the wastewater was 20 mg/L. The wastewater contained elevated concentrations of cadmium and copper. Matrix spike analyses yielded good recoveries (>20%) for all metals except copper, iron, and silver. For copper and iron, the sample concentrations were greater than four times the spike concentration, resulting in 0% recovery. With the matrix spike analysis of silver, the spike was either diluted out or diluted to a concentration near the detection limit.

Ford Electronics and Refrigeration Corporation--

On May 11, 1989, PEI collected a raw F019 filter cake sample at Ford Electronics and Refrigeration Corporation, Connersville, Indiana. PEI's laboratory in Cincinnati, Ohio, performed all of the chemical analyses. Table 15 presents the analytical data for the F019 filter cake. The total cyanide level of the waste filter cake was 2470 µg/g. The waste also contained an elevated concentration of nonpurgeable organics (19,400 µg/g) and fluoride (1980 µg/g). Metal analyses of the sample revealed elevated concentrations of chromium (10,700 µg/g) and silicon (2970 µg/g). Matrix spike and spike duplicate (MS/MSD) analyses yielded good recoveries (>20%) for all the metals except chromium (VI) and copper. Cyanide recoveries were also less than 20 percent. Table 16 presents the results of TCLP leachate analyses for the F019 waste. Elevated TCLP leachate levels were detected for total chromium (116 mg/L). The TCLP levels were above the 20 percent OSWER OA objectives for all the constituents analyzed except cyanide, for which two separate analyses yielded zero recoveries.

BENCH-SCALE TESTING

This section presents results obtained from the autoclave oxidation testing of F006, F007, and F019 wastes. (See Subsection 3.2 for details on Zimpro's autoclave unit.)

Amerock

The Amerock F007 waste received by Zimpro/Passavant for wet-air-oxidation testing had a chemical oxygen demand (COD) of approximately 33 g/L and contained 15.85 g/L suspended solids, which were black. The raw waste contained a total cyanide concentration of 23,667 ppm and an amenable cyanide concentration of 21,750 ppm. An initial autoclave oxygen demand (AOD) of 96 g/L was determined for the waste, and a dilution of 1:1 was needed for testing. Table 17 presents analyses of the autoclave off-gases. Tables 18 and 19 show the analytical results of the dilute raw waste and the filtrate and solids from each autoclave oxidation condition.

TABLE 14. SUMMARY OF MASTER LOCK F009 ANALYSES

Parameter	Concentration, mg/L[a]	Analytical spike recovery, %	Matrix spike recovery, %
Antimony	ND0.5/ND0.5	109	139/150[b]
Arsenic	0.007/0.007	75	69/71[c]
Barium	ND0.05/ND0.05	100	97
Beryllium	ND0.05/ND0.05	99	178/176[b]
Cadmium	85/82	103	0/0[d]
Chromium	0.2/0.2	103	100
Copper	71/62	103	0/0[d]
Iron	12/8	102	0/0[d]
Lead	0.006/0.006	62	69/67
Mercury	0.0003/0.0003	--	92
Nickel	0.8/0.7	104	92
Selenium	ND0.025/ND0.025	88	80
Silver	ND0.1/ND0.1	97	0/0[b]
Thallium	ND0.004/ND0.004	28/24[c]	29/30[c]
Vanadium	ND0.1/ND0.1	99	110
Zinc	2.0/2.0	114	100
pH	12.38/12.39 SU		
Cyanide, amenable	2.5/7.9		448/69[c]
Cyanide, total	20/21		90
Hexavalent chromium	0.16/0.16		63/64
Settleable matter	33		

(continued)

TABLE 14 (continued)

Parameter	Concentration, mg/L[a]	Analytical spike recovery, %	Matrix spike recovery, %
Total residue	10,000/10,000		
Residue: filterable at 180°C	9000/9000		
Residue: nonfilterable at 180°C	790/800		

[a] Except as otherwise noted.

[b] The matrix spike has either been diluted out or was diluted to a concentration near the detection limit.

[c] The spike was prepared and analyzed in duplicate to confirm matrix interferences.

[d] The sample concentration is greater than four times the spike concentration.

TABLE 15. ANALYSIS OF FORD F019 FILTER CAKE

Parameter	Ford F019 filter cake[a]	Spike recoveries, %	
		MS[b]	MSD[c]
Soil pH, SU	8.62		
Ammonia-N	191	79.7	60.5
Cyanide total	2,470	3.2	0.0
Cyanide amenable	d		
Fluoride	1,980	92.8	95.2
NPOC	19,400	e	e
POC	7.76	e	e
Moisture, %	79.8		
Chloride	14.9	67.7	90.3
Nitrate-N	81.0	92.8	104.0
Antimony	<3.48	93.6	93.8
Arsenic	9.05	88.0	152.0
Barium	21.3	91.2	96.6
Beryllium	0.09	78.3	80.0
Boron	25.7	84.3	85.5
Cadmium	7.24	76.4	77.9
Chromium, VI	3.76	8.6	9.1
Chromium, total	10,700	139.4	139.1
Copper	1.19	8.2	10.8
Iron	1,481	131.7	132.1
Lead	<2.61	90.6	91.8
Mercury	0.19	86.3	79.1
Nickel	1.65	22.3	20.5
Selenium	<0.08	45.3	49.7
Silicon	2,970	129.3	134.2
Silver	<0.30	78.1	79.7
Thallium	<4.08	80.3	83.7
Vanadium	6.69	55.9	52.7
Zinc	31,400	103.3	100.1

[a] ug/g unless otherwise indicated.

[b] MS = Matrix spike.

[c] MSD = Matrix spike duplicate.

[d] Because of an interference in the sample, cyanide amenable to chlorination could not be determined.

[e] Not requested.

TABLE 16. ANALYSIS OF FORD F019 TCLP EXTRACTS

Parameter	Ford F019 filter cake, mg/L	Spike recoveries, %	
		MS[a]	MSD[b]
Cyanide, total	0.89	0.0[c]	0.0[c]
Antimony	0.070	95.5	93.7
Arsenic	0.11	106.7	118.7
Barium	0.34	93.7	93.9
Beryllium	0.001	77.4	77.4
Cadmium	0.31	79.4	79.6
Chromium, VI	0.97	99.5	98.3
Chromium, total	116	104.9	105.3
Copper	0.020	93.2	94.7
Iron	1.25	76.9	77.4
Lead	0.052	81.6	82.6
Mercury	0.0012	106.3	107.5
Nickel	0.072	78.8	78.1
Selenium	0.002	30.1	26.4
Silver	0.006	80.2	81.2
Thallium	0.082	81.5	86.0
Vanadium	0.050	77.4	77.0
Zinc	1180	107.6	107.4

[a] MS = Matrix spike.

[b] MSD = Matrix spike duplicate.

[c] The cyanide analyses were performed twice with the same lack of recovery for the spikes.

TABLE 17. AMEROCK F007 WET-AIR-OXIDATION RESULTS

Parameter	Dilute waste	Test runs 1	2	3
Oxidation temperature, °C	-	200	240	280
Time at temperature, min.	-	60	60	60
Oxygen uptake, g/liter	16.685[a]	7.48	16.12	24.49
Percent of feed COD	-	44.8	96.6	146.8
Offgas THC, ppm	-	9	12	9
Offgas CH_4, ppm	-	0.5	0.7	0.3
Suspended solids, g/liter	-	9.5	9.0	8.8

[a] COD of dilute wastewater.

A COD reduction of 79 to 86 percent was observed compared with the dilute waste. Total cyanide was reduced by 99.0 percent at 200°C and 99.5 percent at 280°C. The amenable cyanide concentration in the raw waste was reported as 92 percent of the total cyanide value. Amenable and total cyanide were equal in all filtrate samples. Total solids and total ash decreased with increasing oxidation temperature. Significant ammonia-nitrogen (NH_3-N) was produced from cyanide oxidation at 200°C, whereas much lower NH_3-N concentrations were found at higher temperatures. Oxidation of ammonia to nitrogen gas and water apparently occurs at higher temperatures. No significant amount of sulfide was present in the raw waste.

About 65 percent of the solids in each oxidized sample consisted of ash. Total cyanide analysis of the solids showed 183 µg/g (ppm) total cyanide associated with the solids from the 200°C oxidation. Of this amount, 78 percent was amenable cyanide (143 µg/g). At 9.5 g/liter solids concentration, the solids would contribute only 1.7 mg/L total cyanide to the 117 mg/liter value for the filtrate. Total cyanide destruction would remain at 99.0 percent when both filtrate and solids are considered together. The total cyanide and amenable cyanide contents of the solids from the 240° and 280°C oxidations were below the detection limit of 1.0 µg/g. The solids essentially contribute nothing to total cyanide values for the oxidized wastes. Total cyanide destruction remained at 99.3 and 99.5 percent when both filtrate and solids are considered together.

In general, the concentration of metals in the filtrates (soluble) decreased with increasing oxidation temperature. The major metal species identified were copper and zinc. Generally, the total mass of a metal species accounted for in the filtrate and solids from an oxidation condition ranged from 30 to 90 percent of the input from the dilute raw waste.

TABLE 18. POLLUTANT ANALYSES OF TREATED AMEROCK F007

Parameter	Raw waste	Dilute waste[a]	200°C		240°C		280°C	
			Filtrate	Solids	Filtrate	Solids	Filtrate	Solids
COD, mg/L	33,370	16,685	3,060	-	2,315	-	3,578	-
COD reduction, %	-	-	81.7	-	86.1	-	78.6	-
Cyanide (T), mg/L	23,667	11,834	117	183 µg/g	86	<1.0 µg/g	58	<1.0 µg/g
Cyanide (T), red., %	-	-	99.0	-	99.3	-	99.5	-
Cyanide (A), mg/L	21,750	10,875	114	143 µg/g	86	<1.0 µg/g	55	<1.0 µg/g
Cyanide (A), red., %	-	-	99.0	-	99.2	-	99.5	-
Total solids, mg/L	260,770	130,385	110,000	9500[b]	86,600	9000[b]	76,200	8800[b]
Total ash, mg/L	242,300	121,150	103,600	8300[b]	83,100	8100[b]	66,600	7800[b]
pH	10.8	-	9.8	-	9.4	-	9.0	-
NH_3-N, mg/L	134	67	5,000	-	3,104	-	1,187	-
Sulfide, mg/L	1.36	0.68	-	-	-	-	-	-

[a] Concentrations calculated on 1:1 dilution of raw wastewater.

[b] Concentration of suspended solids/suspended ash filtered from oxidized waste.

TABLE 19. METALS ANALYSES OF TREATED AMEROCK F007

Parameter	Raw waste, mg/L	Dilute waste, mg/L[a]	200°C Filtrate, mg/L	200°C Solids, µg/g	200°C Filtrate, mg/L	200°C Solids, µg/g	200°C Filtrate, mg/L	200°C Solids, µg/g
Arsenic	<1.2	<1.2	<1.2	<35	<1.2	<35	<1.2	<32
Barium	3.23	1.62	0.017	104	0.012	83.4	0.003	68.0
Cadmium	<0.04	<0.04	<0.004	<1.15	<0.004	<1.15	<0.004	<1.07
Chromium (T)	7.5	3.75	3.24	30.5	3.33	13.5	3.04	13.3
Chromium (+6)	<0.1	<0.1	0.90	IS	0.66	<3.4	0.18	<3.9
Copper	7663	3832	863	261,440	553	234,600	316	219,450
Lead	0.81	0.40	2.3	464	1.4	229	0.80	172
Mercury	0.0048	0.0024	0.0095	0.23	0.0106	0.14	0.0106	0.153
Nickel	8.46	4.23	0.38	1,305	0.099	408	0.067	337
Selenium	31.2	15.6	13.0	90	9.2	89	5.5	116
Silver	<0.05	<0.05	<0.05	<1.4	<0.05	<1.4	<0.05	<1.3
Zinc	4180	305	305	75,890	159	79,270	29.8	82,565

[a] Concentrations calculated on 1:1 dilution of raw wastewater.

[b] IS = Insufficient sample.

Ford

The F019 waste received by Zimpro/Passavant for WAO testing was analyzed at a COD of 43 g/liter and 5000 mg/kg total cyanide. A dilution of 1:4 waste to water was determined to be needed for proper testing of the F019 waste stream. Table 20 presents results of the off-gas analyses for the WAO autoclave runs.

TABLE 20. F019 WET-AIR-OXIDATION RESULTS

Sample description	Dilute waste	Products from oxidation		
Oxidation temperature, °C	-	200	240	280
Time at temperature, min.	-	60	60	60
Oxygen uptake, g/L	10.5[a]	3.28	7.08	9.07
Percent of feed COD	-	31.2	67.4	86.4
Off-gas THC, ppm	-	<5	<5	<5
Off-gas CH_4, ppm	-	<1	<1	<1
Suspended solids, g/L	-	39.9	21.6	31.5
Suspended ash, g/L	-	33.1	17.2	28.3

[a] COD of dilute wastewater.

Analytical results for the dilute raw waste and the filtrate and solids for each autoclave oxidation condition are presented in Table 21. A 68 to 83 percent COD reduction was observed compared with the dilute waste. Analysis of the dilute feed yielded only 293 mg/L total cyanide, rather than the approximately 1250 mg/L total cyanide expected. The reason for this discrepancy is unknown. Basing the data on the 293 mg/L cyanide value, total cyanide was reduced by 98 percent at 200°C and 99.9 percent at 280°C. Amenable cyanide concentration in the raw waste was 82.2 percent of the total cyanide. Only the solids from the 240°C oxidation contained significant cyanide (3.07 mg/L). Ammonia-nitrogen (NH_3-N) produced from cyanide oxidation reached a maximum of about 760 mg/liter at the 280° oxidation. No significant amount of sulfide or fluoride was present in the raw waste.

The solids in each sample dried easily and contained approximately 80 to 90 percent ash. Total and amenable cyanide analyses of the solids showed 142 µg/g cyanide associated with the solids from the 240°C oxidation. At 21.6 g/L solids concentration, the solids would contribute only 3.07 mg/L total cyanide to the 0.058 mg/L value for the filtrate. Total cyanide destruction remains near 99 percent when both the filtrate and solids are considered together. The total cyanide and amenable cyanide content of the solids from the 200° and 280°C oxidations contribute less than 1 mg/L cyanide. Even when filtrate and solids are considered together, cyanide destruction was 98 to 99 percent for all temperatures investigated. In general, the concentration of metals in the filtrates (soluble) changed little with increasing oxidation temperature.

TABLE 21. WET-AIR-OXIDATION RESULTS FOR PEI ASSOCIATES, INC., CYANIDE COATING WASTE SLUDGE (F019)

Parameter	Autoclave feed	Oxidized product					
		Filtrate	Cake	Filtrate	Cake	Filtrate	Cake
Analytical No.	19639	19770	19773	19771	19774	19772	19775
Oxidation temperature, °C	-	200	200	240	240	280	280
Time at temperature, min	-	60	60	60	60	60	60
COD, g/L	10.5	1.75	73.7	3.04	160	2.12	25.3
COD reduction, %	-	83.3	-	68		-	79
pH, SU	8.54	7.95	-	7.9	-	7.8	-
NH_3-N, mg/L	27.7	527.50	-	668		-	766
Total solids, g/L except as noted	41.7	2.78	98.8%	2.55	100%	2.08	100%
Total ash, g/L except as noted	28.1	1.45	83.9%	1.26	79.6%	1.35	89.7%
Cyanide, total, mg/L except as noted	293.1	5.07	22.9 µg/g	0.058	142 µg/g	0.133	18 µg/g
Total CN from solids, mg/L	-	-	0.91	-	3.07	-	0.57
Total cyanide reduction, %	-	98	-	99.9	-	99.9	-
Cyanide amenable, mg/L except as noted	240.9	5	22.9 µg/g	0.02	142 µg/g	0.02	18 µg/g
Amenable CN from solids, mg/L	-	-	0.91	-	3.07	-	0.57
Amenable CN reduction, %	-	98	-	>99.9	-	>99.9	-

(continued)

TABLE 21 (continued)

Parameter	Autoclave feed, mg/L	Oxidized product					
		Filtrate, mg/L	Cake, µg/g	Filtrate, mg/L	Cake, µg/g	Filtrate, mg/L	Cake, µg/g
Sulfides	<1	<1	-	<1	-	<1	-
Fluoride	38.9	24.7	0.17	30.9	0.15	38.9	0.23
Arsenic	0.080	0.132	114	0.221	135	<0.005	109
Antimony	<0.005	<0.005	465	<0.005	460	<0.005	469
Barium	2.7	0.21	138	0.35	145	0.77	166
Beryllium	0.007	0.001	0.32	0.001	0.29	<0.01	0.32
Cadmium	2.11	0.013	102	0.007	99	<0.04	104
Chromium(T)	1231	1.92	72,767	1.86	68,590	24	74,072
Copper	0.355	0.053	48.7	0.046	34	0.12	66
Iron	189	0.13	12,000	0.08	11,034	0.08	15,238
Lead	14.7	0.003	816	0.008	586	0.916	584
Mercury	0.0004	0.0011	<0.02	0.0010	<0.02	0.008	0.02
Nickel	0.875	0.007	46	0.011	43	0.21	48
Selenium	0.051	0.250	20	<0.005	<20	<0.005	20
Silver	<0.01	<0.005	<0.5	<0.005	<0.5	<0.05	0.5
Thallium	<0.14	0.010	<5	0.005	<5	0.005	5
Vanadium	0.31	0.006	<0.5	<0.005	<0.5	<0.05	0.5
Zinc	4902	4.6	61,000	4.6	257,000	15.2	279,000

Master Lock

The Master Lock F006 waste for WAO testing contained a COD of 37,000 mg/L and 400 mg/L total cyanide. The COD of the waste required a 1:10 dilution, so the sludge was spiked with potassium hexacyanoferrate III to raise the cyanide content back to about 350 mg/liter. Table 22 shows the results of off-gas testing.

TABLE 22. MASTER LOCK WET-AIR-OXIDATION RESULTS

Sample description	Dilute waste	Products from oxidation		
Oxidation temperature, °C	-	200	240	280
Time at temperature, min.	-	60	60	60
Oxygen uptake, g/L	3.7[a]	0.67	1.55	3.27
Percent of feed COD	-	18.1	41.9	88.4
Off-gas THC, ppm	-	<5	<5	<5
Off-gas CH_4, ppm	-	<1	<1	<1
Suspended solids, g/L	-	14.8	17.9	15.4
Suspended ash, g/L	-	12.6	15.5	13.5

[a] COD of dilute wastewater.

Table 23 presents the results of the raw waste and the filtrate and solids from each autoclave oxidation condition. A COD reduction of 91 to 95 percent was observed compared with the dilute waste. Cyanide recovery from the spiked waste slurry was only 122 mg/L, or about 35 percent. This recovery was based on the 315 mg/L cyanide added by the spiking compound plus 40 mg/L cyanide from the diluted sludge itself. Amenable cyanide concentration in the spiked diluted sludge was 74 mg/L, or 60 percent of the recovered total cyanide value. Amenable and total cyanide concentrations were equal in all filtrate and solids samples. Based on the 122 mg/L total cyanide value for the raw spiked slurry, total cyanide was reduced by 78 percent at 200°C and by 99+ percent at 240° and 280°C. Ammonia-nitrogen produced from the cyanide oxidation reached a maximum of about 300 mg/L for the 240° and 280°C oxidations. No significant amount of sulfide or fluoride was present in the raw waste.

The solids contained approximately 85 percent ash. Total and amenable cyanide analysis of the solids showed 102 µg/g total cyanide associated with the solids from the 200°C oxidation. At 14.8 g/L solids concentration, the solids would contribute only 1.5 mg/L total cyanide to the 26.3 mg/L value for the filtrate. Total cyanide destruction, therefore, remains near 78 percent when both the filtrate and solids are considered together. The total and amenable cyanide content of the solids from the 240° and 280°C oxidations contribute about 1 mg/liter cyanide, which is approximately equal to the cyanide concentration in the filtrates obtained. Even when the filtrate and

TABLE 23. WET-AIR-OXIDATION RESULTS FOR MASTER LOCK CYANIDE COATING WASTE SLUDGE (F006)

Parameter	Autoclave feed	Oxidized product					
		Filtrate	Cake	Filtrate	Cake	Filtrate	Cake
Analytical No.	18320	17341	17344	17342	17345	17343	17346
Oxidation temperature, °C	-	200	200	240	240	280	280
Time at temperature, min.	-	60	60	60	60	60	60
COD, g/L	3.7	0.166	197	0.269	24	0.311	29
COD reduction, %	-	95.5	-	93	-	92	-
pH	11	9.9	-	9.7	-	10.1	-
NH_3-N, mg/L	-	203.60	-	305.1	-	306	-
Total solids, g/L	17.3	1.92	100%	1.25	100%	1.79	100%
Total ash, g/L except as noted	15.9	1.77	85.3%	1.17	86.6%	1.79	87.8%
Cyanide, total, mg/L except as noted	122.4	26.3	102 µg/g	0.82	20 µg/g	1.1	81 µg/g
Total cyanide reduction, %	-	78	-	99	-	99	-
Cyanide amenable, mg/L except as noted	73.9	26.3	102 µg/g	0.82	20 µg/g	1.1	81 µg/g
Amenable CN reduction, %	-	64	-	99	-	98	-

(continued)

TABLE 23 (continued)

Parameter	Autoclave feed, mg/L	Oxidized product					
		Filtrate, mg/L	Cake, µg/g	Filtrate, mg/L	Cake, µg/g	Filtrate, mg/L	Cake, µg/g
Sulfides	<1	<1	-	<1	-	<1	-
Fluoride	3.59	2.12	690	1.8	700	3.5	630
Arsenic	<0.0012	<0.005	<2400	<.005	<2400	<0.005	2400
Antimony	<0.005	<0.005	72.8	<0.005	84.8	<0.005	81.4
Barium	0.54	0.17	40	0.17	43	0.19	39
Beryllium	<0.01	0.018	0.28	0.014	<0.2	0.015	<0.2
Cadmium	220.5	0.53	241,000	0.25	254,000	0.27	241,000
Chromium (T)	348.4	44.4	29,000	16.7	31,000	<0.09	32,000
Chromium (+6)	Interference	33.8	1980	15.3	830	<0.2	73
Copper	729.1	25.9	78,000	5.4	85,000	5.9	79,000
Iron	1177	0.73	9500	0.07	10,100	0.08	9700
Lead	1.12	<0.5	48	<0.5	103	<0.5	127
Mercury	0.0004	0.0021	1.1	0.0051	0.12	0.00411	0.12
Nickel	643.9	2.4	62,000	0.12	63,000	0.33	62,000
Selenium	<0.0002	0.0038	<4000	0.019	<4000	0.036	<4000
Silver	<0.05	<0.05	<1	<0.05	<1	<0.05	<1
Thallium	<0.005	0.040	<14	0.050	<14	0.040	<14
Vanadium	<0.05	<0.05	<1	<0.05	<1	<0.05	<1
Zinc	355.1	0.44	33,000	0.26	35,000	0.29	33,000

solids are considered together, cyanide destruction was 99 and 98 percent, respectively, at 280°C.

IITRI UV/O_3 Testing

On March 16, 1989, PEI collected three 30-gallon drums of F009 waste from the Master Lock Company in Milwaukee, Wisconsin. IITRI received one drum of the waste and began UV/O_3 testing on June 6, 1989. The IITRI analysis of the raw waste showed total cyanide levels of 62.5 ppm. Operational problems caused delays throughout testing. The 1-L reactor, which housed a 1.9-watt medium-pressure lamp, was broken after the first experimental run, which forced the premature use of the 5.0-watt medium-pressure lamp. IITRI did not have any other 1-L reactors, and procurement of a new reactor would have taken several weeks. The Work Plan called for four runs with the 1.9-watt lamp that were not performed. As a result, four additional runs were made with the 5.0-watt lamp. Table 24 summarizes the UV/O_3 experiments conducted by IITRI. A maximum of 65 percent cyanide reduction (62.5 to 22 ppm) was obtained during testing. Larger spiked quantities of iron cyanides proved to be even more difficult to treat, with only 10 percent cyanide reduction (1355 to 1170 ppm) after 4 hours of treatment, which could be considered an excessive time period for treatment. After completion of these experiments, IITRI believed the UV/O_3 reactor system may not have been properly set up (see Figure 8). The rate of the ozone decomposition is extremely fast at an elevated temperature of 65°C; therefore, no residual ozone may have been present when the waste stream reached the separate UV reactor. This could account for the apparent comparability of the treatment effectiveness between ozone and UV/ozone test runs. A separate run (Run 15) conducted by IITRI at a later date introduced the ozone directly into the UV reactor, however, and gave comparable results.

PILOT-SCALE TESTING RESULTS AND DISCUSSION

Introduction

Two pilot-scale testing sessions (March 1988 and June 1988) were conducted on Amerock F007 electroplating waste. The initial pilot runs in March showed system fouling problems; therefore, full runs could not be accomplished. Lessons learned from this session, however, helped to achieve good operation during the June runs.

The second testing was conducted on June 6 and 7, 1988, at the pilot plant facilities of Zimpro/Passavant. The WAO study was performed on the F007 wastes, which contained total cyanides in excess of 30 g/L (3 percent). The 24-hour study was conducted in a 5.4-gal pilot unit constructed of titanium. The major oxidation operating parameters for this test were:

Reactor temperature	454°F
Reactor pressure	1700 psig
Reactor residence time	54 minutes

TABLE 24. SUMMARY OF EXPERIMENTS - OZONE/UV TREATMENT OF CYANIDE WASTE

Run	Waste volume, L	pH	Temperature, °C	UV output, watts	O_3, wt.%	Gas flow, L/min	Time, h	Sparger type[a]	Complex cyanide as CN^-, mg/L		Analysis delay, h[b]
									Feed	Product	
1	6	10.5-11.8	65-40	1.9	3.5	0.5	1	SS	60, 62.5	53	190
2	6	10.6-12	66-38	3.5	3.0	0.5	1	SS		49	190
3	6	10.6	66-63	3.5	3.0	0.5	1	SS		53	170
4	6	10.4	62-66	5.0	3.0	0.5	1	SS		36	145
4a	5						2	SS		25	145
5	6	10.8-11.3	22-27	5.0	3-3.1	0.5	1.1	SS		49	48
6	6	9-8.5	66-64	5.0	3.0	0.5	0.5	SS		44	48
7	6	8	66	5.0	3	0.5-0.2	1.1	SS		37	145
8	6	8	66	5.0	0	0	1	SS		63	24
9	6	8	62-68	0	3	0.5	1	SS		22, 27	260
10	6	8	66	5.0	2.5-4	0.5-0.25	1	SS	1355	1170	260
11	7	8	67-64	0	3.9-3.1	0.5	1	gl		39	0
12	6	10.9	65	0	3.2[c]	0.5	2	gl		67	24[b]
13a	5						4	gl		67	24[b]
13	6	10.5	66	5.0	3.1	0.5	4	gl	1890	1690	24[b]
15	2	10.5	65-79	5.0	3.0	0.5	2	gl	60	22	0

[a] SS = stainless steel spargers; gl = glass spargers.

[b] Preserved by bubbling air, adding ascorbic acid, and adjusting pH to 12.

[c] Ozone measured 1.6% at outlet.

For details concerning the Zimpro/Passavant wet-air-oxidation treatment system refer to Section 3.2. Table 25 contains the analyses of the oxidized liquor.

Results

The cyanide destruction as shown by the contractor's analyses is very high, 99.991 percent, with a residual cyanide concentration in the oxidized liquor of 1.57 ppm. A loose, brown, sand-like deposit was found at the bottom of the reactor, which indicates that these solids were held in suspension in the reactor during operation. The primary metal components of this material are zinc, sodium, phosphorus, and copper. A scale deposit was also found on the reactor walls, the primary metal components of which are copper, sodium, and phosphorus. Both deposits contain 5 to 10 percent carbonate.

Analysis of the caustic scrubber solution used during the run revealed it to contain less than 1.0 mg/liter of cyanide. This indicates that the off-gas cyanide concentration was less than 0.08 ppm. The off-gases were analyzed for ammonia and total hydrocarbons (THC) and found to contain 0.71 percent ammonia and 15 ppm THC. No specific hydrocarbon compounds could be detected in the off-gas.

FULL-SCALE TESTING - ELECTROLYTIC OXIDATION

Table 26 presents data obtained during Versar's sampling visit to the Woodward Governor Company on October 7, 1987. Amenable cyanide levels were reduced by 48 percent after 1 day of treatment and by 91 percent after full electrolytic treatment. In combination with alkaline chlorination, a reduction of 99.5 percent in amenable cyanide was achieved. Total cyanide was reduced by 43 percent after 24 hours of treatment and by 91 percent after full treatment. Alkaline chlorination further reduced cyanide levels by 97 percent of the original feed. The COD levels were reduced by 73.5 percent after electrolytic oxidation.

STABILIZATION/SOLIDIFICATION TESTING

This subsection summarizes the results and conclusions obtained from the bench-scale stabilization/solidification testing of F006, F011, and F012 wastes. Stabilization/solidification was performed on three F006 wastes generated by John Deere and Company in Waterloo, Iowa; Amerock Corporation in Rockford, Illinois; and Master Lock Company in Milwaukee, Wisconsin. The F011 and F012 wastes were both generated at Woodward Governor Company in Rockford, Illinois.

F006 Waste

As discussed in Section 5, three binders were used in the stabilization/solidification of the F006 wastes: portland cement, lime/fly ash, and kiln dust. After allowing the mixture to cure for 28 days, the optimum binder-to-waste ratio for each binder was selected based on unconfined compressive strength tests. Selected samples were subjected to the TCLP, and extracts were analyzed for the parameters listed in Table 27.

TABLE 25. RESULTS OF FOO7 CYANIDE RUN

Parameter	Oxidized sample
pH	9.7
Total solids	185.0 g/L
Total ash, 600°C	-
Suspended solids	0.18 g/L
Suspended ash	-
COD	2.54 g/L
NH_3-N	4527 mg/L
Cl	147 mg/L
Total P	1.7 g/L
SO_4-S	0.45 g/L
CO_2	42.4 g/L
CN, total	1.57 mg/L
NO_2-N	142 mg/L
NO_3-N	3484 mg/L
Cu	1.05 g/L
Zn	0.005 g/L
Na	67.8 g/L
Fe	6.0 mg/L
Specific gravity	1.164

TABLE 26. ANALYTICAL RESULTS FOR METALS AND INORGANIC PARAMETERS - WOODWARD GOVERNOR ELECTROLYTIC OXIDATION (mg/L)

Parameter	Electrolytic oxidation reactor			Alkaline chlorination reactor after treatment
	Before treatment	After 24 h of treatment	After full treatment	
Antimony	0.029	-[a]	0.283	0.021
Arsenic	1.23	-	1.4	0.188
Barium	1.0	-	2.37	0.495
Beryllium	0.0012	-	0.0014	0.0072
Cadmium	0.01	-	0.057	0.004
Chromium (hexavalent)	0.01	-	0.01	23.4
Chromium (total)	5.42	-	57.8	16.7
Copper	1.03	-	0.469	0.225
Lead	1.1	-	3.61	0.672
Mercury	0.00025	-	0.028	0.00027
Nickel	2.88	-	2.62	8.06
Selenium	0.123	-	0.28	0.05
Silver	0.0072	-	0.0028	0.002
Thallium	0.123	-	0.56	0.10
Vanadium	0.156	-	0.784	0.805
Zinc	0.338	-	1.27	0.187
Cyanide (amenable)	5,350[b]	2800	473	26
Cyanide (total)	5,350	3030	484	153
Total solids	197,000	-	304,000	83,500
Total suspended solids	38,400	-	-	25,500
Chemical oxygen demand	7,140	-	1,890	-
Total organic carbon	19,500	-	24,600	-
Oil and grease	11.0	-	15.1	-

(continued)

TABLE 26 (continued)

Parameter	Electrolytic oxidation reactor			Alkaline chlorination reactor after treatment
	Before treatement	After 24 h of treatment treatment	After after treatment	
Carbonate	87,000	-	-	-
Chloride	21,300	-	-	-
Fluoride	5.55	-	-	-
Iron	27.8	-	168	122
Potassium	18,500	-	25,900	4,320
Sodium	32,200	-	37,800	10,300
Sulfate	90.5	-	-	-
Sulfide	1.0	-	-	-

[a] - = Not analyzed.

[b] Result may be high because of analytical interference.

TABLE 27. LIST OF TCLP ANALYTES BY WASTE CODE

Analyte	F006				Woodward Governor	
	Deere	Amerock	Master Lock		F011	F012
Cyanide (T)		x			x	
Cyanide (A)		x			x	
Aluminum	x	x	x	x	x	x
Antimony	x	x	x	x	x	x
Arsenic	x	x	x	x	x	x
Barium	x	x	x	x	x	x
Beryllium	x	x	x	x	x	x
Cadmium	x	x	x	x	x	x
Calcium	x	x	x	x	x	x
Chromium (T)	x	x	x	x	x	x
Chromium (+6)	x	x	x	x	x	x
Cobalt	x	x	x	x	x	x
Copper	x	x	x	x	x	x
Iron	x	x	x	x	x	x
Lead	x	x	x	x	x	x
Magnesium	x	x	x	x	x	x
Manganese	x	x	x	x	x	x
Mercury	x	x	x	x	x	x
Molybdenum	x	x	x	x	x	x
Nickel	x	x	x	x	x	x
Selenium	x	x	x	x	x	x
Silver	x	x	x	x	x	x
Sodium	x	x	x	x	x	x
Thallium	x	x	x	x	x	x
Tim	x	x	x	x	x	x
Vanadium	x	x	x	x	x	x
Zinc	x	x	x	x	x	x

Analytical results for the Deere and Company TCLP extracts showed low residual concentrations of cadmium, hexavalent chromium, and nickel, which are the metals used as the basis for listing F006. Complexed cyanide is another hazardous constituent for which F006 is listed; however, John Deere and Company does not use cyanide in their processes; therefore, cyanide is not expected in their F006 waste. Many of the other metals listed in Table 27 also were present in very low concentrations. Calcium and sodium were the only metals found in high concentrations; however, this was attributed to the binders. The only notable difference in the effectiveness of the binders was that the zinc concentrations were much higher in the kiln dust extracts than in the cement or lime/fly ash extracts. Zinc concentrations in the cement and lime/fly ash extracts were nondetectable (less than 0.02 mg/L) to 0.83 mg/L, whereas the concentrations in the kiln dust extracts ranged from 2.6 to 3.2 mg/L.

The analytical results obtained from the Amerock TCLP extracts are listed in Tables 28 through 35. Amerock stabilization/solidification TCLP data showed low concentrations of metals in the extracts for all three binders. Cadmium, which is not used at the plant, was nondetectable at 0.003 mg/L in all TCLP extracts, hexavalent chromium ranged from 0.04 to 0.23 mg/L, and nickel was nondetectable (0.025 and 0.042 mg/L) in all TCLP extracts. The cement binder was noted to be more effective in containing copper and zinc. Average TCLP extract concentrations of copper and zinc with the cement binder were 0.83 and 0.20 mg/L, respectively; the lime/fly ash binder extracts showed an average of 7.36 mg/L copper and 2.63 mg/L zinc, and the kiln dust binder extracts showed an average of 5.89 mg/L copper and 3.13 mg/L zinc.

Total cyanide was nondetectable at 0.02 mg/L in the lime/fly ash and kiln dust extracts; however, it was detected at an average concentration of 0.39 mg/liter in the cement binder extracts.

The TCLP extracts of the Master Lock stabilized/solidified F006 waste did not demonstrate the same level of effectiveness (in terms of extract quality) as did the John Deere and Amerock wastes. Table 36 shows the analytical results obtained from the Master Lock TCLP leachates. With the kiln dust binder, extracts contained 42.2 to 77.5 mg/L cadmium, 0.054 to 0.078 mg/L hexavalent chromium, 4.63 to 11.3 mg/L nickel, and 106 to 112 mg/L magnesium. The cement and lime/fly ash binders were much more effective than the kiln dust binder. The cement binder extracts showed 0.26 to 0.28 mg/L cadmium, 0.023 to 0.074 mg/L hexavalent chromium, nickel at below detectable limits (0.031 mg/L), and 0.096 to 0.13 mg/L magnesium. The lime/fly ash binder extracts showed 0.031 to 0.17 mg/L cadmium, 0.30 to 0.37 mg/L hexavalent chromium, nondetectable (0.031 mg/L) nickel, and 1.04 to 3.47 mg/L magnesium.

It can be concluded from these tests that the stabilization/solidification process is an effective technology for containing metals in F006 waste; however, binder selection may have a significant impact on the quality of the TCLP extract. This was clearly demonstrated earlier in this section with the John Deere, Amerock, and Master Lock F006 wastes and the portland cement,

TABLE 28. ANALYTICAL DATA SUMMARY OF UNTREATED AMEROCK F006 WASTE

PARAMETER	TOTAL WASTE ANALYSIS (ug/g) *	TCLP LEACHATES (mg/l)			MEAN **	STD DEV ***	REL STD DEV ****
		A	B	C			
CYANIDE (T) @	CBI	< 0.02	< 0.02	< 0.02			
CYANIDE (A) @@	CBI	NA	NA	NA			
pH s.u.	CBI						
CHLORIDE	CBI						
MOISTURE (%)	CBI						
OIL & GREASE	CBI						
SULFATE	CBI						
SULFIDE	CBI						
TOC	CBI						
ALUMINUM		0.065	0.067	0.08	0.071	0.006649	9.366167
ANTIMONY	CBI	2.09	2.11	2.11	2.1	0.009428	0.448956
ARSENIC	CBI	0.005	0.006	0.006	0.006	0.000471	7.856742
BARIUM	CBI	< 0.002	< 0.002	< 0.002			
BERYLLIUM	CBI	< 0.002	< 0.002	< 0.002			
CADMIUM	CBI	0.029	0.029	0.029	0.029		
CALCIUM		798	812	769	793	17.90716	2.258154
CHROMIUM (t)	CBI	0.012	0.012	0.14	0.055	0.060339	109.7086
CHROMIUM (+6)	CBI	< 0.006	0.011	0.013			
COBALT	CBI	< 0.023	0.026	< 0.023			
COPPER	CBI	138	130	136	135	3.399346	2.518034
IRON	CBI	< 0.023	< 0.023	< 0.023			
LEAD	CBI	< 0.001	< 0.001	< 0.001			
MAGNESIUM		302	291	279	291	9.392668	3.227721
MANGANESE		1.88	1.91	1.9	1.9	0.012472	0.656431
MERCURY	CBI	< 0.0003	< 0.0003	< 0.0003			
MOLYBDENUM	CBI	0.19	0.19	0.17	0.18	0.009428	5.237828
NICKEL	CBI	26.7	26.8	26.8	26.8	0.047140	0.175897
SELENIUM	CBI	0.91	0.99	0.99	0.96	0.037712	3.928371
SILVER	CBI	< 0.006	< 0.006	< 0.006			
SODIUM		52.3	49.3	49.6	50.4	1.349073	2.676733
THALLIUM	CBI	< 0.004	< 0.004	< 0.004			
TIN		< 0.103	< 0.103	< 0.103			
VANADIUM	CBI	< 0.008	< 0.008	< 0.008			
ZINC	CBI	248	244	239	244	3.681787	1.508929

NA - Not analyzable by Method 9010 - matrix interference
** - Arithmetic mean of TCLP leachate data
*** - Standard deviation
**** - Relative standard deviation
@ - Total cyanide
@@ - Cyanide amenable to alkaline clorination
CBI - Confidential business information

TABLE 29. TOTAL WASTE ANALYSIS OF UNTREATED AND TREATED AMEROCK F006 WASTE

PARAMETER	UNTREATED F006 (ug/g)	TREATED F006 (ug/g)		
		WET-14-CEM-19	WET-14-KD-0.7	WET-14-LF-44
pH, s.u.	CBI	12.25	12.28	12.31
CHLORIDE	CBI	402	1520	241
MOISTURE (%)	CBI	29.6	36.9	40.1
OIL & GREASE	CBI	1200	1370	750
SULFATE	CBI	725	3510	43
SULFIDE	CBI	44	56	56
TOC	CBI	5690	11600	17400
ANTIMONY	CBI	< 5.61	65.8	72.1
ARSENIC	CBI	23	9.25	16.8
BARIUM	CBI	86.3	51	115
BERYLLIUM	CBI	< 0.10	0.49	1.34
CADMIUM	CBI	0.66	1.41	0.9
CHROMIUM (T)	CBI	213	336	349
CHROMIUM (+6)	CBI	0.62	< 0.60	< 0.60
COBALT	CBI	3.94	2.56	4.9
COPPER	CBI	3130	6470	6620
LEAD	CBI	6.2	14.6	9.35
MERCURY	CBI	0.3	< 0.14	< 0.14
MOLYBDENUM	CBI	< 4.42	< 4.42	5.48
NICKEL	CBI	325	567	591
SELENIUM	CBI	24.1	59.5	32.8
SILVER	CBI	< 0.27	< 0.27	< 0.27
THALLIUM	CBI	< 0.21	< 0.21	< 0.21
VANADIUM	CBI	29.2	12	29.1
ZINC	CBI	3600	6120	6240

CBI - Confidential business information

TABLE 30. TCLP ANALYSIS RESULTS OF 28-DAY AMEROCK F006/CEMENT BINDER TEST SAMPLES

PARAMETER	TCLP LEACHATES			MEAN	STD DEV	REL STD DEV
	A	B	C			
CYANIDE (T)	0.48	0.37	0.32	0.39	0.066833	17.13669
CYANIDE (A)	0.34	0.22	0.18	0.25	0.067986	27.19477
ALUMINUM	0.04	0.014	< 0.023			
ANTIMONY	0.094	< 0.076	< 0.076			
ARSENIC	0.002	0.002	0.003	0.002	0.000471	23.57022
BARIUM	0.85	0.92	0.97	0.91	0.049216	5.408360
BERYLLIUM	< 0.001	< 0.001	< 0.001			
CADMIUM	< 0.003	< 0.003	< 0.003			
CALCIUM	2510	2560	2600	2557	36.81787	1.439885
CHROMIUM (T)	0.21	0.2	0.18	0.2	0.012472	6.236095
CHROMIUM (+6)	0.16	0.17	0.23	0.19	0.030912	16.26950
COBALT	< 0.010	< 0.010	< 0.010			
COPPER	0.89	0.81	0.8	0.83	0.040276	4.852628
IRON	0.65	0.053	0.047	0.25	0.282853	113.1413
LEAD	0.004	0.006	0.007	0.006	0.001247	20.78698
MAGNESIUM	0.069	0.049	0.053	0.057	0.008640	15.15962
MANGANESE	< 0.001	< 0.001	< 0.001			
MERCURY	< 0.0012	< 0.0006	< 0.0003			
MOLYBDENUM	0.062	0.104	0.081	0.082	0.017172	20.94186
NICKEL	< 0.025	< 0.025	< 0.025			
SELENIUM	0.012	0.014	0.012	0.013	0.000942	7.252377
SILVER	< 0.004	< 0.004	< 0.004			
SODIUM	31.6	28.7	28.9	29.7	1.322455	4.452712
THALLIUM	< 0.004	< 0.004	< 0.004			
TIN	< 0.105	< 0.105	< 0.105			
VANADIUM	< 0.007	< 0.007	< 0.007			
ZINC	0.17	0.19	0.25	0.2	0.033993	16.99673

TABLE 31. TCLP ANALYTICAL RESULTS OF 28-DAY AMEROCK FOO6/LIME/FLY ASH BINDER TEST SAMPLES

PARAMETER	TCLP LEACHATES			MEAN	STD DEV	REL STD DEV
	A	B	C			
CYANIDE (T)	< 0.02	< 0.04	< 0.02			
CYANIDE (A)	< 0.02	< 0.02	< 0.02			
ALUMINUM	< 0.022	< 0.022	0.029			
ANTIMONY	< 0.112	< 0.112	< 0.112			
ARSENIC	< 0.002	0.002	0.002			
BARIUM	0.586	0.64	0.56	0.6	0.033319	5.553332
BERYLLIUM	< 0.002	< 0.002	< 0.002			
CADMIUM	< 0.003	< 0.003	< 0.003			
CALCIUM	3790	2670	2510	2923	613.0434	20.97308
CHROMIUM (T)	0.089	0.084	0.079	0.084	0.004082	4.860098
CHROMIUM (+6)	0.056	0.042	0.049	0.049	0.005715	11.66423
COBALT	0.014	< 0.014	< 0.014			
COPPER	6.76	7.61	7.71	7.36	0.426223	5.791083
IRON	< 0.023	< 0.023	< 0.023			
LEAD	0.023	0.018	0.016	0.019	0.002943	15.49431
MAGNESIUM	0.043	0.035	0.071	0.05	0.015434	30.86889
MANGANESE	< 0.002	< 0.002	< 0.002			
MERCURY	< 0.0003	< 0.003	< 0.0003			
MOLYBDENUM	0.142	0.128	0.186	0.152	0.024711	16.25767
NICKEL	< 0.042	< 0.042	< 0.042			
SELENIUM	0.131	0.131	0.085	0.116	0.021684	18.69362
SILVER	< 0.006	< 0.006	< 0.006			
SODIUM	30.1	32.9	34	32.3	1.641814	5.083017
THALLIUM	< 0.004	< 0.004	< 0.004			
TIN	< 0.103	< 0.103	< 0.103			
VANADIUM	< 0.014	< 0.014	< 0.014			
ZINC	2.57	2.61	2.71	2.63	0.058878	2.238722

TABLE 32. TCLP ANALYTICAL RESULTS OF 28-DAY AMEROCK F006/KILN DUST BINDER TEST SAMPLES

PARAMETER	TCLP LEACHATES			MEAN	STD DEV	REL STD DEV
	A *	B	C			
CYANIDE (T)	< 0.04	< 0.04	< 0.04			
CYANIDE (A)	< 0.04	< 0.04	< 0.04			
ALUMINUM	< 0.022	< 0.022	< 0.022			
ANTIMONY	< 0.062	< 0.062	< 0.062			
ARSENIC	< 0.002	0.002	0.002			
BARIUM	0.39	0.4	0.48	0.42	0.040276	9.589719
BERYLLIUM	< 0.002	< 0.002	< 0.002			
CADMIUM	< 0.003	< 0.003	< 0.003			
CALCIUM	2771	2960	3040	2993	112.7839	3.768258
CHROMIUM (t)	0.11	0.11	0.12	0.12	0.004714	3.928371
CHROMIUM (+6)	0.114	0.084	0.077	0.09	0.016048	17.83170
COBALT	< 0.014	< 0.014	< 0.014			
COPPER	5.67	5.99	5.57	5.89	0.179133	3.041319
IRON	< 0.015	< 0.015	< 0.015			
LEAD	0.03	0.03	0.033	0.03	0.001414	4.714045
MAGNESIUM	0.005	< 0.002	< 0.002			
MANGANESE	< 0.002	< 0.002	< 0.002			
MERCURY	< 0.0003	0.0003	< 0.0003			
MOLYBDENUM	0.12	0.13	0.13	0.13		
NICKEL	< 0.025	< 0.025	< 0.025			
SELENIUM	0.058	0.067	0.054	0 06	0.005436	9.060836
SILVER	< 0.009	< 0.009	< 0.009			
SODIUM	45	43.7	42.5	44.8	1.020892	2.278778
THALLIUM	< 0.004	< 0.004	< 0.004			
TIN	< 0.37	< 0.37	< 0.37			
VANADIUM	< 0.014	< 0.014	< 0.014			
ZINC	3.06	2.99	3.1	3.13	0.045460	1.452415

* During the TCLP, the kiln dust 'A' sample was extracted at a ratio of 1:18.6 (190g of waste to 3530 mL of extraction fluid # 2) rather than 1 : 20 (190g of waste to 3800 ml of fluid); therefore, analytical data for sample "A" was mathematically corrected by multiplying the laboratory reported value by 0.93 to obtain the value representative of 1:20 dilution. Detected values shown in this table for sample 'A' have all been corrected.

TABLE 33. WET ANALYTICAL RESULTS OF 28-DAY AMEROCK F006/CEMENT BINDER TEST SAMPLES

PARAMETER	WET LEACHATES			MEAN	STD DEV	REL STD DEV
	A	B	C			
ANTIMONY	1.2	2	1.9	1.7	0.355902	20.93544
ARSENIC	0.08	0.071	0.073	0.075	0.003858	5.144816
BARIUM	2.2	5.2	3.6	3.7	1.225651	33.12572
BERYLLIUM	< 0.05	< 0.05	< 0.05			
CADMIUM	0.15	0.24	0.23	0.21	0.040276	19.17943
CHROMIUM (T)	3.2	4.3	4.2	3.9	0.496655	12.73475
CHROMIUM (+6)	0.07	0.07	0.07	0.07		
COBALT	0.3	0.5	0.5	0.4	0.094280	23.57022
COPPER	170	250	260	227	40.27681	17.74309
LEAD	0.029	0.055	0.03	0.038	0.012027	31.65196
MERCURY	< 0.0002	< 0.0002	< 0.0002			
MOLYBDENUM	0.5	0.8	0.8	0.7	0.141421	20.20305
NICKEL	4	5.9	5.7	5.2	0.852447	16.39322
SELENIUM	< 0.025	< 0.025	< 0.025			
SILVER	0.2	0.3	0.3	0.3	0.047140	15.71348
THALLIUM	< 0.004	< 0.004	< 0.004			
VANADIUM	1.4	1.8	1.9	1.7	0.216024	12.70733
ZINC	42	54	54	50	5.656854	11.31370

TABLE 34. WET ANALYTICAL RESULTS OF 28-DAY AMEROCK F006/LIME/FLY ASH BINDER TEST SAMPLES

PARAMETER	WET LEACHATES			MEAN	STD DEV	REL STD DEV
	A	B	C			
ANTIMONY	2.5	3.1	3.1	2.9	0.282842	9.753196
ARSENIC	0.1	0.19	0.18	0.16	0.040276	25.17301
BARIUM	0.63	0.91	1.4	0.98	0.318224	32.47186
BERYLLIUM	< 0.05	< 0.05	< 0.05			
CADMIUM	0.07	0.08	0.07	0.07	0.004714	6.734350
CHROMIUM (T)	3.9	4.6	4.5	4.3	0.309120	7.188851
CHROMIUM (+6)	0.04	0.04	0.04	0.04		
COBALT	0.1	0.1	< 0.1			
COPPER	440	550	600	530	66.83312	12.61002
LEAD	0.027	0.036	0.032	0.032	0.003681	11.50558
MERCURY	< 0.0008	0.0008	0.0008			
MOLYBDENUM	1	1.2	1.3	1.2	0.124721	10.39349
NICKEL	13	12	12	12	0.471404	3.928371
SELENIUM	2.6	3.1	3.3	3	0.294392	9.813067
SILVER	0.2	0.2	0.2	0.2		
THALLIUM	< 0.004	< 0.004	< 0.004			
VANADIUM	0.4	0.4	0.4	0.4		
ZINC	42	62	70	58	11.77568	20.30289

TABLE 35. WET ANALYTICAL RESULTS OF 28-DAY AMEROCK F006/KILN DUST BINDER TEST SAMPLES

PARAMETER	A	B	C	MEAN	STD DEV	REL STD DEV
ANTIMONY	3.6	1.4	1.6	2.1	0.899382	42.82773
ARSENIC	0.038	0.045	0.046	0.043	0.003559	8.276804
BARIUM	2.3	0.33	0.4	1.01	0.912615	90.35794
BERYLLIUM	< 0.05	< 0.05	< 0.05			
CADMIUM	0.15	0.06	0.07	0.09	0.040276	44.75202
CHROMIUM (T)	7.5	3.2	4	4.9	1.867261	38.10738
CHROMIUM (+6)	0.15	0.14	0.14	0.14	0.004714	3.367175
COBALT	0.2	< 0.1	0.1			
COPPER	720	290	380	463	185.1725	39.99408
LEAD	0.22	0.26	0.16	0.21	0.041096	19.56956
MERCURY	< 0.0008	< 0.0008	< 0.0008			
MOLYBDENUM	1.2	0.5	0.6	0.77	0.309120	40.14553
NICKEL	17	7.2	8.4	10.9	4.364503	40.04131
SELENIUM	2.3	3.1	3.4	2.9	0.464279	16.00964
SILVER	0.3	0.1	0.2	0.2	0.081649	40.82482
THALLIUM	< 0.02	< 0.004	< 0.004			
VANADIUM	0.5	0.2	0.3	0.3	0.124721	41.57397
ZINC	75	100	94	90	10.65624	11.84027

TABLE 36. ANALYTICAL RESULTS OF MASTER LOCK F006 TCLP LEACHATES

Parameter	Raw F006 (mg/l)		
	TCLP-F006(2)[a]-RAW-A	TCLP-F006(2)-RAW-B	TCLP-F006(2)-RAW-C
Aluminum	0.057	0.096	0.088
Antimony	0.079	<0.070	<0.070
Arsenic	0.003	0.002	0.002
Barium	0.42	0.41	0.34
Beryllium	<0.002	<0.002	<0.002
Cadmium	1304	1340	1250
Calcium	654	708	733
Chromium, VI	<0.006	0.007	0.011
Chromium, total	0.74	0.65	0.59
Cobalt	<0.017	0.020	<0.017
Copper	16.0	15.8	14.2
Iron	<0.013	<0.013	0.021
Lead	<0.001	<0.001	<0.001
Magnesium	172	176	172
Manganese	4.58	4.62	4.53
Mercury	0.0006	0.0006	<0.0006
Molybdenum	<0.044	<0.044	<0.044
Nickel	257	261	248
Selenium	<0.002	<0.002	<0.002
Silver	<0.006	<0.006	<0.006
Sodium	85.6	124	89.1
Thallium	<0.003	<0.003	<0.003
Tin	0.17	0.21	0.17
Vanadium	<0.012	<0.012	<0.012
Zinc	93.0	90.5	81.7

[a] "(2)" refers to the second F006 waste stabilized at WES under Work Assignment Nos. 1-9 and 2-9. Under Contract No. 68-03-3389 this was the third F006 waste stabilized at WES.

TABLE 36 (continued)

Parameter	F006 treated with kiln dust (mg/l)		
	TCLP-F006(2)-KD-1-A	TCLP-F006(2)-KD-1-B	TCLP-F006(2)-KD-1-C
Aluminum	0.055	0.061	0.053
Antimony	<0.070	<0.070	0.091
Arsenic	0.002	0.002	<0.002
Barium	0.29	0.31	0.27
Beryllium	<0.002	<0.002	<0.002
Cadmium	42.2	72.9	77.5
Calcium	1640	1580	1605
Chromium, VI	0.078	0.054	0.059
Chromium, total	0.079	0.065	0.069
Cobalt	0.022	<0.017	<0.017
Copper	0.40	0.52	0.54
Iron	<0.013	0.034	<0.013
Lead	<0.001	<0.001	<0.001
Magnesium	106	111	112
Manganese	0.64	1.06	1.15
Mercury	0.0008	0.0007	<0.0006
Molybdenum	<0.044	<0.044	<0.044
Nickel	4.63	10.4	11.3
Selenium	0.002	0.002	<0.002
Silver	<0.006	<0.006	<0.006
Sodium	154	131	137
Thallium	<0.003	<0.003	<0.003
Tin	<0.062	<0.062	<0.062
Vanadium	<0.012	<0.012	<0.012
Zinc	0.80	1.46	1.65

TABLE 36 (continued)

Parameter	F006 treated with cement (mg/l)		
	TCLP-F006(2)-CEM-3-A	TCLP-F006(2)-CEM-3-B	TCLP-F006(2)-CEM-3-C
Aluminum	0.39	0.36	0.49
Antimony	<0.070	<0.070	0.071
Arsenic	0.002	<0.002	0.002
Barium	0.37	0.40	0.34
Beryllium	<0.002	<0.002	<0.002
Cadmium	0.28	0.29	0.26
Calcium	1740	1740	1810
Chromium, VI	0.037	0.074	0.023
Chromium, total	0.43	0.43	0.47
Cobalt	<0.017	<0.017	<0.017
Copper	0.25	0.26	0.27
Iron	0.98	0.80	1.32
Lead	<0.001	<0.001	<0.001
Magnesium	0.13	0.096	0.10
Manganese	<0.002	<0.002	<0.002
Mercury	<0.0006	0.0006	0.0011
Molybdenum	<0.044	<0.044	<0.044
Nickel	<0.031	<0.031	<0.031
Selenium	0.002	0.002	<0.002
Silver	<0.006	0.019	<0.006
Sodium	100	99.8	104
Thallium	<0.003	<0.003	<0.003
Tin	0.13	0.17	0.064
Vanadium	<0.012	<0.012	<0.012
Zinc	0.067	0.13	0.081

TABLE 36 (continued)

Parameter	F006 treated with lime/flyash (mg/l) TCLP-F006(2)-LF-11-A	TCLP-F006(2)-LF-11-B	TCLP-F006(2)-LF-11-C
Aluminum	<0.024	<0.024	<0.024
Antimony	<0.070	<0.070	<0.070
Arsenic	<0.002	<0.002	<0.002
Barium	0.36	0.33	0.28
Beryllium	<0.002	<0.002	<0.002
Cadmium	0.17	0.031	0.051
Calcium	1590	1590	1550
Chromium, VI	0.35	0.37	0.30
Chromium, total	0.29	0.28	0.28
Cobalt	<0.017	<0.017	<0.017
Copper	0.23	0.22	0.19
Iron	0.17	0.12	0.13
Lead	<0.001	<0.001	<0.001
Magnesium	1.43	1.04	3.47
Manganese	<0.002	<0.002	<0.002
Mercury	<0.0012	<0.0012	<0.0012
Molybdenum	<0.044	<0.044	<0.044
Nickel	<0.031	<0.031	<0.031
Selenium	<0.002	<0.002	<0.002
Silver	<0.006	<0.006	<0.006
Sodium	146	159	139
Thallium	<0.003	<0.003	<0.003
Tin	<0.062	<0.062	<0.062
Vanadium	<0.012	<0.012	<0.012
Zinc	0.11	0.082	0.073

lime/fly ash, and kiln dust binders. Portland cement was found to be effective in containing all metals in the wastes and producing a relatively clean extract. Lime/fly ash was very effective on the John Deere Waste F006 waste; however, concentrations of zinc and copper in the Amerock extracts and magnesium in the Master Lock extracts were somewhat elevated. The kiln dust binder was not as effective as the cement and lime/fly ash binders. With the John Deere F006, the kiln dust failed to bind the zinc effectively; with the Amerock F006, both zinc and copper appeared in the TCLP extracts at elevated concentrations; and with the Master Lock F006, cadmium was detected in high concentrations.

Stabilization/solidification was shown to be an effective technology for containing cyanide in the Amerock F006 waste when bound in lime/fly ash.

F011 Waste

The basis for listing F011 is cyanide (salts). No metals were identified as a basis for listing. The analytical results obtained from the F011 TCLP extracts are presented in Tables 37 through 44. On a total waste analysis basis, the F011 waste collected at Woodward Governor contained 17.2, 4.23, 81.6, 4.76, 535, 5.79, and 31.6 µg/g total chromium, cobalt, copper, lead, nickel, vanadium, and zinc, respectively. Untreated F011 average TCLP concentrations were reported to be 0.37, 37.6, and 2.45 mg/L barium, magnesium, and nickel, respectively. Others were at low or nondetectable concentrations.

Cement-treated F011 TCLP extracts showed average concentrations of 0.3, 45.8, and 2.66 mg/L barium, magnesium, and nickel, respectively. Lime/fly ash extracts had average TCLP concentrations of 0.29, 34.5, and 2.06 mg/L barium, magnesium, and nickel, respectively. Kiln dust extracts had average TCLP concentrations of 0.2, 37.1, and 3.21 mg/L barium, magnesium, and nickel, respectively. As these data indicate, little if any reduction in pollutant concentrations was evident in the treated versus the untreated F011. Because of the contributions of the binder constituents, some of the treated samples actually showed higher concentrations than did the untreated samples.

Total cyanide concentrations in the treated F011 TCLP leachates averaged 1.8 mg/L with the cement binder, 0.49 mg/L with the lime/fly ash binder, and from nondetectable (0.05 mg/L) to 0.17 mg/L with the kiln dust binder.

A comparison of the TCLP data for the untreated F011 extracts with the data for treated F011 extracts indicates that stabilization/solidification is not an effective technology for F011 waste.

F012 Waste

The basis for listing F012 is cyanide (complexed). No metals were identified as a basis for listing. The analytical results obtained from the F012 TCLP extracts are presented in Tables 45 through 52. The F012 waste

TABLE 37. ANALYTICAL DATA SUMMARY OF UNTREATED F011 WASTE

PARAMETER	TOTAL WASTE ANALYSIS (ug/g) *	TCLP LEACHATES (mg/l)			MEAN **	STD DEV ***	REL STD DEV ****
		A	B	C			
pH, s.u.	12.42						
CHLORIDE	639						
MOISTURE , (%)	30.1						
OIL & GREASE	5						
SULFATE	16800						
SULFIDE	32						
TOC	239						
ALUMINUM		0.094	0.085	0.072	0.084	0.009030	10.75096
ANTIMONY	< 22.6	< 0.076	0.079	< 0.076			
ARSENIC	1.95	0.002	< 0.002	< 0.002			
BARIUM	19.8	0.36	0.39	0.35	0.37	0.016996	4.593711
BERYLLIUM	< 0.27	< 0.001	< 0.001	< 0.001			
CADMIUM	< 0.81	0.009	0.008	0.008	0.008	0.000471	5.892556
CALCIUM		2320	2360	2310	2330	21.60246	0.927144
CHROMIUM (T)	17.2	0.23	0.14	0.081	0.15	0.061266	40.84417
CHROMIUM (+6)	0.12	0.16	0.17	0.12	0.15	0.021602	14.40164
COBALT	4.23	< 0.010	< 0.010	< 0.010			
COPPER	81.6	0.05	0.053	0.045	0.049	0.003299	6.734350
IRON		0.68	0.2	0.054	0.31	0.267413	86.26256
LEAD	4.76	< 0.001	< 0.001	< 0.001			
MAGNESIUM		37.7	40.5	34.7	37.63	2.368309	6.293673
MANGANESE		0.55	0.58	0.57	0.57	0.012472	2.188103
MERCURY	< 0.14	< 0.0006	< 0.0003	< 0.0003			
MOLYBDENUM	< 11.1	< 0.037	< 0.037	< 0.037			
NICKEL	535	2.41	2.56	2.37	2.45	0.081785	3.338188
SELENIUM	< 0.08	0.002	0.003	< 0.002			
SILVER	< 1.20	< 0.004	< 0.004	< 0.004			
SODIUM		82.4	80.9	74.2	79.2	3.564952	4.501203
THALLIUM	< 0.21	< 0.004	< 0.004	< 0.004			
TIN		< 0.11	< 0.11	< 0.11			
VANADIUM	5.79	< 0.007	< 0.007	< 0.007			
ZINC	31.6	0.26	0.25	0.27	0.26	0.008164	3.140371

NA - Not analyzable by Method 9010 - matrix interference
* - Except as otherwise noted
** - Arithmetic mean of TCLP leachate data
**** - Relative standard deviation
*** - Standard deviation

TABLE 38. TOTAL WASTE ANALYSIS OF UNTREATED AND TREATED F011 WASTE

PARAMETER	UNTREATED F011 (ug/g) *	TREATED F011 (ug/g) *					
		WET-12-CEM-1	WET-12-CEM-4	WET-12-KD-1	WET-12-KD-4	WET-12-LF-11	WET-12-LF-33
pH, s.u.	12.42	12.5	12.62	12.71	12.58	12.58	12.63
CHLORIDE	639	449	160	760	780	472	381
MOISTURE %	30.1	29.9	20.4	30.5	22.1	28.5	21.8
OIL & GREASE	5	5	< 5.0	254	5	243	10
SULFATE	16800	14900	14200	13900	13400	14000	13000
SULFIDE	32	22	20	32	32	22	20
TOC	239	851	1720	401	4390	3060	5780
ANTIMONY	< 22.6	< 22.6	< 22.6	< 22.6	< 22.6	< 22.6	< 22.6
ARSENIC	1.95	2.6	6.75	3.05	5.55	8.1	15.8
BARIUM	19.8	30.6	56	26	55.1	44	99.4
BERYLLIUM	< 0.27	< 0.27	< 0.27	< 0.27	0.68	0.51	1.35
CADMIUM	< 0.81	0.81	< 0.81	< 0.81	< 0.81	1.38	< 0.81
CHROMIUM (+6)	0.12	0.23	2.32	< 0.06	< 0.06	0.23	< 0.06
CHROMIUM (T)	17.2	20.7	29.9	18.6	17	18.8	19.6
COBALT	4.23	< 3.06	5.76	< 3.06	7.14	< 3.06	6.57
COPPER	81.6	75.1	64.7	72.2	72.4	69.6	67
LEAD	4.76	3.71	4.41	4.88	6.98	4.91	4.82
MERCURY	< 0.14	< 0.14	< 0.14	< 0.14	< 0.14	< 0.14	< 0.14
MOLYBDENUM	< 11.1	< 11.1	< 11.1	< 11.1	< 11.1	< 11.1	< 11.1
NICKEL	535	443	359	447	405	383	366
SELENIUM	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08
SILVER	< 1.20	< 1.20	< 1.20	< 1.20	< 1.20	< 1.20	< 1.20
THALLIUM	< 0.21	< 0.21	< 0.21	0.21	< 0.21	< 0.21	< 0.21
VANADIUM	5.79	10.8	19.2	8.91	16.1	13.9	28.7
ZINC	31.6	38.8	38.5	37.9	33.1	46.4	32.7

* Except as otherwise noted

TABLE 39. TCLP ANALYTICAL RESULTS OF 28-DAY F011/CEMENT BINDER TEST SAMPLES

PARAMETER	TCLP LEACHATES (mg/l) A	B	C	MEAN	STD DEV	REL STD DEV
CYANIDE (T) *	1.08	2.25	2.06	1.8	0.512661	28.48121
CYANIDE (A) **	NA	NA	NA			
ALUMINUM	< 0.023	< 0.023	0.023			
ANTIMONY	< 0.076	< 0.076	< 0.076			
ARSENIC	< 0.002	0.002	0.002			
BARIUM	0.26	0.31	0.33	0.3	0.029439	9.813067
BERYLLIUM	< 0.001	< 0.001	< 0.001			
CADMIUM	< 0.003	< 0.003	< 0.003			
CALCIUM	2320	2490	2440	2416.66	71.33644	2.951861
CHROMIUM (+6)	0.45	0.36	0.33	0.38	0.050990	13.41847
CHROMIUM (T)	0.26	0.21	0.21	0.227	0.023570	10.38335
COBALT	< 0.010	< 0.010	< 0.010			
COPPER	0.029	0.027	0.022	0.026	0.002943	11.32277
IRON	0.76	0.68	0.72	0.72	0.032659	4.536092
LEAD	< 0.001	< 0.001	< 0.001			
MAGNESIUM	46.4	47	44.1	45.8	1.249888	2.729015
MANGANESE	0.048	0.049	0.047	0.048	0.000816	1.701034
MERCURY	0.002	0.0024	0.0021	0.0022	0.000169	7.725787
MOLYBDENUM	< 0.037	< 0.037	< 0.037			
NICKEL	2.82	2.66	2.5	2.66	0.130639	4.911257
SELENIUM	< 0.002	< 0.002	< 0.002			
SILVER	0.01	0.007	0.006	0.008	0.001699	21.24591
SODIUM	63.2	56.3	57.7	59.1	2.978067	5.039032
THALLIUM	< 0.004	< 0.004	0.007			
TIN	0.16	0.18	0.17	0.17	0.008164	4.802921
VANADIUM	0.022	0.024	0.024	0.023	0.000942	4.099169
ZINC	0.11	0.17	0.14	0.14	0.024494	17.49635

* - Total cyanide
** - Cyanide amenable to alkaline chlorination
NA - not analyzable by Method 9010 - matrix interference

TABLE 40. TCLP ANALYTICAL RESULTS OF 28-DAY F011/LIME/FLY ASH BINDER TEST SAMPLES

PARAMETER	TCLP LEACHATES (mg/l)					
	A	B	C	MEAN	STD DEV	REL STD DEV
CYANIDE (T)	0.45	0.19	0.81	0.49	0.254209	51.87939
CYANIDE (A)	*	< 0.05	< 0.05			
ALUMINUM	< 0.023	< 0.023	< 0.023			
ANTIMONY	< 0.076	< 0.076	< 0.076			
ARSENIC	0.004	0.005	0.002	0.004	0.001247	31.18047
BARIUM	0.23	0.24	0.4	0.29	0.077888	26.85821
BERYLLIUM	< 0.001	< 0.001	< 0.001			
CADMIUM	< 0.003	< 0.003	< 0.003			
CALCIUM	2330	2930	2870	2710	269.8147	9.956263
CHROMIUM (+6)	0.21	0.11	0.09	0.14	0.052493	37.49527
CHROMIUM (T)	0.12	0.098	0.098	0.105	0.010370	9.877047
COBALT	0.013	< 0.010	< 0.010			
COPPER	< 0.018	0.029	0.032			
IRON	0.38	0.32	0.32	0.34	0.028284	8.318903
LEAD	< 0.001	< 0.001	0.005			
MAGNESIUM	32.5	33.5	37.5	34.5	2.160246	6.261585
MANGANESE	0.24	0.26	0.26	0.26	0.009428	3.626188
MERCURY	0.0013	0.0003	0.003	0.0024	0.001114	46.43959
MOLYBDENUM	0.045	0.061	0.061	0.056	0.007542	13.46870
NICKEL	1.68	2.24	2.24	2.06	0.263986	12.81488
SELENIUM	< 0.002	0.002	< 0.002			
SILVER	0.004	< 0.004	< 0.004			
SODIUM	52.9	68.2	37.9	53	12.37012	23.33985
THALLIUM	< 0.004	< 0.002	< 0.002			
TIN	0.14	< 0.10	< 0.10			
VANADIUM	0.018	0.013	0.013	0.015	0.002357	15.71348
ZINC	0.093	0.17	0.24	0.17	0.060035	35.31480

* interferent in sample

TABLE 41. TCLP ANALYTICAL RESULTS OF 28-DAY F011/KILN DUST BINDER TEST SAMPLES

PARAMETER	TCLP LEACHATES (mg/l)					
	A	B	C	MEAN	STD DEV	REL STD DEV
CYANIDE (T)	0.11	< 0.05	0.17			
CYANIDE (A)	*	< 0.05	< 0.05			
ALUMINUM	< 0.023	0.043	0.12			
ANTIMONY	< 0.076	< 0.076	< 0.076			
ARSENIC	< 0.002	< 0.002	0.002			
BARIUM	0.18	0.25	0.17	0.2	0.035590	17.79513
BERYLLIUM	< 0.001	< 0.001	< 0.001			
CADMIUM	< 0.003	0.004	0.006			
CALCIUM	2400	2980	2870	2750	251.5286	9.146496
CHROMIUM (+6)	0.16	0.07	0.08	0.11	0.040276	36.61529
CHROMIUM (T)	0.077	0.069	0.076	0.074	0.003559	4.809494
COBALT	< 0.010	< 0.010	0.011			
COPPER	0.027	0.044	0.057	0.042	0.012283	29.24686
IRON	0.21	0.089	0.091	0.13	0.056574	43.51879
LEAD	< 0.001	< 0.001	0.001			
MAGNESIUM	38.8	42.6	29.8	37.1	5.367391	14.46736
MANGANESE	0.35	0.32	0.32	0.33	0.014142	4.285495
MERCURY	< 0.0006	< 0.0003	0.0004			
MOLYBDENUM	< 0.037	< 0.037	< 0.037			
NICKEL	1.85	2.45	2.34	2.21	0.260810	11.80138
SELENIUM	0.004	0.005	0.006	0.005	0.000816	16.32993
SILVER	0.007	< 0.004	< 0.004			
SODIUM	67.7	77.5	65.1	70.1	5.339163	7.616495
THALLIUM	< 0.004	< 0.002	< 0.002			
TIN	< 0.105	< 0.10	< 0.10			
VANADIUM	0.018	0.009	0.008	0.012	0.004496	37.47427
ZINC	0.19	0.25	0.37	0.27	0.074833	27.71598

* interferent in sample

TABLE 42. WET ANALYTICAL RESULTS OF 28-DAY F011/CEMENT BINDER TEST SAMPLES

PARAMETER	WET LEACHATES (mg/l) A	B	C	MEAN	STD DEV	REL STD DEV
ANTIMONY	< 0.5	< 0.5	< 0.5			
ARSENIC	0.09	0.04	0.03	0.05	0.026246	52.49338
BARIUM	0.12	0.11	0.09	0.11	0.012472	11.33835
BERYLLIUM	< 0.05	< 0.05	< 0.05			
CADMIUM	< 0.05	< 0.05	< 0.05			
CHROMIUM (t)	1.9	1.8	1.8	1.9	0.047140	2.481076
CHROMIUM (+6)	0.29	0.26	0.25	0.26	0.016996	6.537204
COBALT	0.1	0.1	< 0.1			
COPPER	5.6	5.8	5.8	5.7	0.094280	1.654050
LEAD	< 0.002	< 0.002	< 0.002			
MERCURY	0.0005	0.001	0.0005	0.0006	0.000235	39.28371
MOLYBDENUM	< 0.5	< 0.5	< 0.5			
NICKEL	17	18	16	17	0.816496	4.802921
SELENIUM	< 0.05	< 0.025	< 0.05			
SILVER	0.1	< 0.1	< 0.1			
THALLIUM	< 0.004	< 0.004	< 0.004			
VANADIUM	0.8	0.9	0.7	0.8	0.081649	10.20620
ZINC	0.2	0.2	0.2	0.2		

TABLE 43. WET ANALYTICAL RESULTS OF 28-DAY F011/LIME/FLY ASH BINDER TEST SAMPLES

PARAMETERS	WET LEACHATES (mg/l)					
	A	B	C	MEAN	STD DEV	REL STD DEV
ANTIMONY	0.5	1	0.9	0.8	0.216024	27.00308
ARSENIC	0.1	0.035	0.037	0.057	0.030180	52.94901
BARIUM	0.15	0.16	0.12	0.14	0.016996	12.14052
BERYLLIUM	0.05	0.06	0.05	0.05	0.004714	9.428090
CADMIUM	< 0.05	0.11	0.13			
CHROMIUM (T)	2.2	2.1	1.9	2.1	0.124721	5.939138
CHROMIUM (+6)	0.16	0.14	0.16	0.15	0.009428	6.285393
COBALT	0.1	0.2	0.2	0.16	0.047140	29.46278
COPPER	8.6	7.9	10	8.8	0.873053	9.921061
LEAD	0.002	< 0.01	< 0.01			
MERCURY	0.001	0.0006	0.0026	0.0014	0.000864	61.72133
MOLYBDENUM	0.6	< 0.5	< 0.5			
NICKEL	26	27	29	27	1.247219	4.619330
SELENIUM	0.2	< 0.005	< 0.005			
SILVER	< 0.1	0.2	< 0.5			
THALLIUM	< 0.004	< 0.004	< 0.004			
VANADIUM	1.1	1.1	0.7	0.96	0.188561	19.64185
ZINC	0.4	1.4	1.1	0.96	0.418993	43.64515

TABLE 44. WET ANALYTICAL RESULTS OF 28-DAY F011/KILN DUST BINDER TEST SAMPLES

PARAMETER	WET LEACHATES (mg/l) A	B	C	MEAN	STD DEV	REL STD DEV
ANTIMONY	< 0.5	0.6	0.6			
ARSENIC	0.06	0.078	0.075	0.071	0.007874	11 09015
BARIUM	0.11	0.1	0.12	0.11	0.008164	7.422696
BERYLLIUM	< 0.05	< 0.05	< 0.05			
CADMIUM	< 0.05	0.12	0.11			
CHROMIUM (T)	1.6	1.7	2	1.8	0.169967	9.442628
CHROMIUM (+6)	0.09	0.11	0.09	0.1	0.009428	9.428090
COBALT	< 0.1	0.1	0.1			
COPPER	7.7	7.8	8	7.8	0.124721	1.598998
LEAD	0.01	0.01	0.02	0.01	0.004714	47.14045
MERCURY	< 0.0004	< 0.0002	< 0.0004			
MOLYBDENUM	0.6	< 0.5	< 0.5			
NICKEL	28	28	31	29	1.414213	4.876598
SELENIUM	< 0.025	< 0.025	< 0.025			
SILVER	< 0.1	0.1	0.1			
THALLIUM	< 0.004	< 0.004	< 0.004			
VANADIUM	0.7	0.7	0.8	0.7	0.047140	6.734350
ZINC	1.7	1.1	1.3	1.4	0.249443	17.81741

TABLE 45. ANALYTICAL DATA SUMMARY OF UNTREATED F012 WASTE

PARAMETER	TOTAL WASTE ANALYSIS (ug/g) *	TCLP LEACHATES (mg/l)			MEAN **	STD DEV ***	REL STD DEV ****
		A	B	C			
pH, s.u.	11.84						
CHLORIDE	1200						
MOISTURE (%)	42.3						
OIL & GREASE	66500						
SULFATE	15000						
SULFIDE	24.4						
TOC	1200						
ALUMINUM		0.031	0.023	0.03	0.028	0.003559	12.71080
ANTIMONY	< 3.78	< 0.076	< 0.076	< 0.076			
ARSENIC	5.2	< 0.002	< 0.002	< 0.002			
BARIUM	84.2	0.32	0.34	0.32	0.33	0.009428	2.856997
BERYLLIUM	< 0.05	< 0.001	< 0.001	< 0.001			
CADMIUM	5.9	0.04	0.036	0.032	0.036	0.003265	9.072184
CALCIUM		2750	2620	2530	2633	90.30811	3.429856
CHROMIUM (T)	27.1	0.22	0.25	0.22	0.23	0.014142	6.148754
CHROMIUM (+6)	3.66	0.26	0.21	0.27	0.25	0.026246	10.49867
COBALT	0.82	< 0.010	0.014	0.018			
COPPER	423	0.25	0.23	0.22	0.23	0.012472	5.422691
IRON		0.097	0.078	0.092	0.09	0.008041	8.935065
LEAD	15.9	< 0.001	< 0.001	< 0.001			
MAGNESIUM		42.9	42.6	36.3	40.6	3.043024	7.495135
MANGANESE		0.55	0.55	0.49	0.53	0.028284	5.336654
MERCURY	< 0.18	0.001	< 0.0003	0.0004			
MOLYBDENUM	< 1.86	< 0.037	< 0.037	< 0.037			
NICKEL	848	4.13	4.17	4.13	4.14	0.018856	0.455463
SELENIUM	< 0.08	< 0.002	< 0.002	< 0.002			
SILVER	1.82	< 0.004	< 0.004	< 0.004			
SODIUM		54.9	51.8	43	49.9	5.040502	10.10120
THALLIUM	< 0.12	< 0.002	< 0.002	< 0.002			
TIN		< 0.10	< 0.10	< 0.10			
VANADIUM	6.55	< 0.007	< 0.007	< 0.007			
ZINC	60.7	0.28	0.31	0.31	0.3	0.014142	4.714045

* - Except as otherwise noted
** - Arithmetic mean of TCLP leachate data
**** - Relative standard deviation
*** - Standard deviation

TABLE 46. TOTAL WASTE ANALYSIS OF UNTREATED AND TREATED F012 WASTE

PARAMETER	UNTREATED F012 (ug/g) *	TREATED F012 (ug/g)					
		TCA-F012 -CEM-1	TCA F012 -CEM-25	TCA-F012 -KD-1	TCA-F012 -KD-25	TCA-F012 -LF-1	TCA-F012 -LF-25
pH, S.U.	11.84	11.93	11.91	11.96	11.96	11.99	11.73
CHLORIDE	1200	1030	750	1250	1500	900	750
MOISTURE %	42.3	37.8	32.6	38.8	32	37.9	29.8
OIL & GREASE	66500	62600	64600	64900	730	174	682
SULFATE	15000	14000	13600	16000	15400	14800	16600
SULFIDE	24.4	36.4	10	18.4	< 6.4	4.5	27
TOC	1200	2770	807	953	1120	3550	5640
ANTIMONY	< 3.78	< 3.78	< 3.78	< 3.78	< 3.78	< 3.78	< 3.78
ARSENIC	5.2	5.25	6.95	4.75	7.45	11.6	15.5
BARIUM	84.2	99.4	86	78.1	77.3	81.5	104
BERYLLIUM	< 0.05	< 0.05	< 0.05	< 0.05	0.35	0.65	1.2
CADMIUM	5.9	4.56	4.89	5.34	5.04	4.53	3.71
CHROMIUM (T)	27.1	26.1	31.2	23.6	24.4	23.9	24.8
CHROMIUM (+6)	3.66	2.22	2.33	1.24	1.27	3.24	< 0.055
COBALT	0.82	1.28	1.97	1.34	1.79	2.36	3.63
COPPER	423	313	286	311	278	277	236
LEAD	15.9	14.9	11.5	17.1	12.6	19.4	16
MERCURY	< 0.18	< 0.14	< 0.15	< 0.16	< 0.14	< 0.14	< 0.14
MOLYBDENUM	< 1.86	< 1.86	< 1.86	< 1.86	< 1.86	2.03	2.74
NICKEL	848	596	605	655	573	559	446
SELENIUM	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08
SILVER	1.82	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30
THALLIUM	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12
VANADIUM	6.55	9.54	14.8	7.92	10.8	16.2	24.8
ZINC	60.7	49.7	55.2	59	68	55.3	60.5

* Except as otherwise noted

TABLE 47. TCLP ANALYTICAL RESULTS OF 28-DAY F012/CEMENT BINDER TEST SAMPLES

PARAMETER	TCLP LEACHATES (mg/l)			MEAN	STD DEV	REL STD DEV
	A	B	C			
ALUMINUM	0.044	0.053	< 0.024			
ANTIMONY	< 0.070	< 0.070	< 0.070			
ARSENIC	< 0.002	< 0.002	< 0.002			
BARIUM	0.31	0.36	0.29	0.32	0.029439	9.199750
BERYLLIUM	< 0.001	< 0.001	< 0.001			
CADMIUM	0.004	0.005	0.005	0.005		
CALCIUM	2420	2550	2590	2520	72.57180	2.879833
CHROMIUM (T)	0.16	0.14	0.15	0.15	0.008164	5.443310
CHROMIUM (+6)	0.21	0.37	0.19	0.26	0.080553	30.98216
COBALT	< 0.017	< 0.017	< 0.017			
COPPER	0.094	0.092	0.1	0.095	0.003399	3.578259
IRON	0.032	0.037	0.032	0.034	0.002357	6.932419
LEAD	< 0.001	< 0.001	< 0.001			
MAGNESIUM	47	48.9	46.7	47.5	0.974109	2.050756
MANGANESE	0.27	0.25	0.27	0.26	0.009428	3.626188
MERCURY	< 0.0003	0.0004	< 0.0003			
MOLYBDENUM	< 0.044	< 0.044	< 0.044			
NICKEL	2.73	2.74	2.31	2.6		
SELENIUM	0.002	< 0.002	0.005			
SILVER	< 0.006	< 0.006	< 0.006			
SODIUM	61.8	65.3	63.8	63.6	1.433720	2.254278
THALLIUM	0.004	0.004	0.003	0.004	0.000471	
TIN	< 0.062	< 0.062	< 0.062			
VANADIUM	< 0.012	< 0.012	< 0.012			
ZINC	0.16	0.18	0.16	0.17	0.009428	5.545935

TABLE 48. TCLP ANALYTICAL RESULTS OF 28-DAY F012/LIME/FLY ASH BINDER TEST SAMPLES

PARAMETER	TCLP LEACHATES (mg/l)			MEAN	STD DEV	REL STD DEV
	A	B	C			
ALUMINUM	1.08	0.56	1.4	1.01	0.346153	34.27262
ANTIMONY	< 0.070	< 0.070	< 0.070			
ARSENIC	0.002	0.002	< 0.002			
BARIUM	0.34	0.41	0.34	0.37	0.032998	8.918463
BERYLLIUM	< 0.001	< 0.001	< 0.001			
CADMIUM	< 0.003	< 0.003	< 0.003			
CALCIUM	2250	2240	2300	2263	26.24669	1.159818
CHROMIUM (T)	0.17	0.16	0.17	0.17	0.004714	2.772967
CHROMIUM (+6)	0.21	0.24	0.27	0.24	0.024494	10.20620
COBALT	< 0.017	< 0.017	< 0.017			
COPPER	< 0.021	< 0.021	< 0.021			
IRON	0.02	0.046	< 0.013			
LEAD	0.002	< 0.001	0.002			
MAGNESIUM	5.27	24.9	8.55	12.9	8.585632	66.55529
MANGANESE	< 0.002	0.02	< 0.002			
MERCURY	0.001	0.0005	< 0.0003			
MOLYBDENUM	< 0.044	< 0.044	< 0.044			
NICKEL	< 0.031	0.034	< 0.031			
SELENIUM	< 0.002	< 0.002	< 0.002			
SILVER	< 0.006	< 0.006	< 0.006			
SODIUM	52.3	51.1	51.7	51.7	0.489897	0.947578
THALLIUM	0.007	0.007	0.007	0.007		
TIN	< 0.062	< 0.062	< 0.062			
VANADIUM	< 0.012	< 0.012	< 0.012			
ZINC	0.076	0.1	0.063	0.08	0.015326	19.15760

TABLE 49. TCLP ANALYTICAL RESULTS OF 28-DAY F012/KILN DUST BINDER TEST SAMPLES

PARAMETER	TCLP LEACHATES (mg/l)			MEAN	STD DEV	REL STD DEV
	A	B	C			
ALUMINUM	0.035	0.033	0.027	0.032	0.003399	10.62295
ANTIMONY	< 0.070	< 0.070	< 0.070			
ARSENIC	< 0.002	< 0.002	< 0.002			
BARIUM	0.43	0.37	0.33	0.38	0.041096	10.81476
BERYLLIUM	< 0.001	< 0.001	< 0.001			
CADMIUM	< 0.003	0.004	< 0.003			
CALCIUM	2420	2410	2350	2393	30.91206	1.291770
CHROMIUM (T)	0.25	0.29	0.31	0.29	0.024944	8.601511
CHROMIUM (+6)	0.29	0.34	0.36	0.33	0.029439	8.920970
COBALT	< 0.017	0.026	< 0.017			
COPPER	0.069	< 0.021	< 0.021			
IRON	0.078	0.072	0.048	0.066	0.012961	19.63860
LEAD	0.004	< 0.001	< 0.001			
MAGNESIUM	48.6	45.6	45.9	46.7	1.349073	2.888808
MANGANESE	0.18	0.19	0.15	0.17	0.016996	9.998077
MERCURY	< 0.0003	0.0003	< 0.0003			
MOLYBDENUM	< 0.044	< 0.044	< 0.044			
NICKEL	1.6	1.39	1.43	1.47	0.091043	6.193424
SELENIUM	< 0.002	< 0.002	< 0.002			
SILVER	< 0.006	< 0.006	< 0.006			
SODIUM	63.4	61.2	66.7	63.8	2.260285	3.542766
THALLIUM	< 0.003	0.004	0.003			
TIN	< 0.062	< 0.062	0.11			
VANADIUM	< 0.012	< 0.012	< 0.012			
ZINC	0.15	0.15	0.11	0.14	0.018856	13.46870

TABLE 50. WET ANALYTICAL RESULTS OF 28-DAY F012/CEMENT BINDER TEST SAMPLES

PARAMETER	WET LEACHATES (mg/l)			MEAN	STD DEV	REL STD DEV
	A	B	C			
ANTIMONY	< 2.5	< 2.5	< 2.5			
ARSENIC	< 0.03	< 0.03	0.08			
BARIUM	0.27	< 0.25	< 0.25			
BERYLLIUM	< 0.25	< 0.25	< 0.25			
CADMIUM	< 0.25	< 0.25	< 0.25			
CHROMIUM (T)	2	1.6	2	1.9	0.188561	9.924305
CHROMIUM (+6)	0.4	0.39	0.41	0.4		
COBALT	< 0.5	< 0.5	< 0.5			
COPPER	16	16	14	15.3	0.942809	6.162150
LEAD	< 2.5	< 2.5	< 2.5			
MERCURY	0.0005	< 0.0002	< 0.0002			
MOLYBDENUM	< 0.5	< 0.5	< 0.5			
NICKEL	9	11	6	8.6	2.054804	23.89307
SELENIUM	< 0.05	< 0.05	< 0.05			
SILVER	< 0.5	< 0.5	< 0.5			
THALLIUM	< 0.004	0.004	0.004			
VANADIUM	< 0.5	< 0.5	< 0.5			
ZINC	< 0.5	< 0.5	< 0.5			

TABLE 51. WET ANALYTICAL RESULTS OF 28-DAY F012/LIME/FLY ASH BINDER TEST SAMPLES

PARAMETER	WET LEACHATES (mg/l)			MEAN	STD DEV	REL STD DEV
	A	B	C			
ANTIMONY	< 2.5	< 2.5	< 2.5			
ARSENIC	0.008	0.009	0.005	0.007	0.001699	24.28104
BARIUM	0.29	0.25	0.25	0.27	0.018856	6.983770
BERYLLIUM	< 0.25	< 0.25	< 0.25			
CADMIUM	< 0.25	< 0.25	< 0.25			
CHROMIUM (T)	3	3	2	2.6	0.471404	18.13094
CHROMIUM (+6)	0.49	0.62	0.68	0.6	0.079302	13.21708
COBALT	< 0.5	< 0.5	< 0.5			
COPPER	24	25	23	24	0.816496	3.402069
LEAD	< 2.5	< 2.5	< 2.5			
MERCURY	< 0.0004	< 0.0002	< 0.0002			
MOLYBDENUM	< 0.5	< 0.5	< 0.5			
NICKEL	24	24	19	22	2.357022	10.71373
SELENIUM	< 0.025	< 0.025	< 0.025			
SILVER	< 0.5	< 0.5	< 0.5			
THALLIUM	< 0.004	< 0.004	< 0.004			
VANADIUM	0.6	< 0.5	< 0.5			
ZINC	< 0.5	< 0.5	< 0.5			

TABLE 52. WET ANALYTICAL RESULTS OF 28-DAY F012/KILN DUST BINDER TEST SAMPLES

PARAMETERS	WET LEACHATES (mg/l)			MEAN	STD DEV	REL STD DEV
	A	B	C			
ANTIMONY	< 2.5	< 2.5	< 2.5			
ARSENIC	0.018	0.017	< 0.003			
BARIUM	< 0.25	< 0.25	< 0.25			
BERYLLIUM	< 0.25	< 0.25	< 0.25			
CADMIUM	< 0.25	< 0.25	< 0.25			
CHROMIUM (T)	2	2	2	2		
CHROMIUM (+6)	0.34	0.31	0.31	0.32	0.014142	4.419417
COBALT	< 0.5	< 0.5	< 0.5			
COPPER	27	27	26	26.6	0.471404	1.772197
LEAD	< 2.5	< 2.5	< 2.5			
MERCURY	< 0.0002	< 0.0002	< 0.0002			
MOLYBDENUM	< 0.5	< 0.5	< 0.5			
NICKEL	37	31	33	33.6	2.494438	7.423923
SELENIUM	< 0.025	< 0.025	< 0.025			
SILVER	< 0.5	< 0.5	< 0.5			
THALLIUM	< 0.004	< 0.004	< 0.004			
VANADIUM	< 0.5	< 0.5	< 0.5			
ZINC	< 0.5	< 0.5	< 0.5			

collected at Woodward Governor contained a total waste analysis basis of 5.2, 84.2, 5.9, 27.1, and 3.66 µg/g arsenic, barium, cadmium, chromium, and hexavalent chromium, respectively, and 423, 15.9, 848, 6.55, and 60.7 µg/g copper, lead, nickel, vanadium, and zinc, respectively. (Cyanide analysis was not requested by the Agency.) Untreated F012 average TCLP concentrations were reported to be 40.6 mg/L magnesium and 4.14 mg/L nickel. Other metals were at low or nondetectable concentrations.

Cement-treated F012 TCLP extracts showed average concentrations of 47.5 mg/L magnesium and 2.6 mg/L nickel. Lime/fly ash extracts showed 1.01 mg/L aluminum, 12.9 mg/L magnesium, and nondetectable (0.031 mg/L) to 0.034 mg/L nickel. Kiln dust extracts showed TCLP extract concentrations of 46.7 mg/L magnesium and 1.47 mg/L nickel.

A comparison of the untreated TCLP data with the treated TCLP data indicates that stabilization/solidification with lime/fly ash is very effective for treating nickel and has limited effectiveness in treating magnesium. Cement and kiln dust, however, demonstrated limited effectiveness in containing nickel and had no effect on magnesium.

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APPENDIX

REGULATORY OVERVIEW OF LAND DISPOSAL RESTRICTIONS FOR SELECTED METAL-FINISHING WASTE CODES

Hazardous waste treatment, storage, and disposal practices, formerly controlled under the Clean Water Act or restricted by State regulations, were regulated by the Resource Conservation and Recovery Act (RCRA) when the Act was passed by Congress in 1976. Recognizing that liquid hazardous wastes placed into land disposal units contributed to the formation of uncontrolled toxic and hazardous waste sites, the EPA developed regulations under RCRA restricting their disposal. On November 8, 1984, however, Congress enacted the Hazardous and Solid Waste Amendments (HSWA). A major section of the 1984 amendments to RCRA is the requirement for EPA to set treatment standards for all RCRA hazardous wastes. The treatment standard set by EPA must be met before land disposal is allowed. Treatment standards are based upon the performance of the best demonstrated available technology (BDAT) to treat the waste. The EPA defines "demonstrated" technologies as those currently used treat the waste or hazardous constituent(s) in the waste, or those used to treat wastes or their hazardous constituents that are similar to the waste being evaluated for BDAT. "Available," according to the EPA definition, means that the technology 1) is commercially available, and 2) substantially diminishes the toxicity of the waste or reduces the probability of hazardous constituents migrating from the waste. The amendments also set a congressionally mandated schedule for phasing out the land disposal of all listed and characteristic RCRA hazardous wastes. The HSWA definition of "land disposal" includes disposal into the following types of units: landfills, surface impoundments, waste piles, injection wells, land-treatment units, salt dome formations, salt bed formations, and underground mines or caves [42 USC 6924(k)].

The statutory deadlines mandated by HSWA required EPA to restrict land disposal of hazardous wastes within a limited time frame. The first category of wastes to be banned from land disposal include the F001 through F005 solvents, and dioxin-containing hazardous wastes. Subsequent to the ban of these wastes, EPA restricted the "California list" wastes, which include certain hazardous wastes containing metals, free cyanides, PCBs, low-pH wastes, and liquid and nonliquid wastes containing halogenated organic compounds (HOCs) above specified levels. All other listed RCRA wastes were separated into thirds, based on volume and toxicity. The so-called "First-Third" listed hazardous wastes were restricted from land disposal on August 8, 1988; the "Second-Third" were restricted from land disposal on June 8, 1989; and the "Third-Third", along with all characteristic wastes, were restricted from land disposal in May 1990 (see Table A-1).

TABLE A-1. SCHEDULE FOR LAND DISPOSAL RESTRICTION REGULATIONS[a]

Chemicals	Effective date of ban	Status
Solvents and dioxins	11/8/86	Promulgated
California list	7/8/87	Promulgated
Scheduled wastes		
First-third	8/8/88	Promulgated
Second-third	6/8/88	Promulgated
Third-third	5/8/90	Pending

[a] Source: U.S. EPA, OSWER.

The HSWA requirements include setting a schedule for treatment standards for all listed and characteristic hazardous wastes. If EPA fails to set treatment standards for any of the listed hazardous wastes, RCRA §3004(g)(6) states that those wastes may be land-disposed only if the following conditions apply: 1) the land-disposal facility is in compliance with the requirements of RCRA §3004(o), which are minimum technology requirements (i.e., double-liner system, leachate-collection system, ground-water monitoring); and 2) prior to disposal, the generator has certified to the Administrator that availability of treatment capacity is insufficient to treat the waste and that land disposal is the only practical alternative available. These provisions are known as the "soft-hammer" provisions.

The land-disposal restriction rules promulgated by EPA define waste treatability groups by waste codes and identify BDAT for each waste code. Treatment standards for each identified treatability group are based on the demonstrated level of treatment achievable by the corresponding BDAT identified for that treatability group. Use of the BDAT identified for each treatability group is not required to meet the concentration-based treatment standards; any technology not otherwise prohibited may be used to achieve the level of treatment required as a prerequisite to land disposal. Dilution of a waste with either aqueous or nonaqueous materials, however, is prohibited as a substitute for meeting or partially meeting the treatment standards.

The wastes evaluated in this report include primarily electroplating wastes containing cyanides; i.e., F006 (wastewater treatment sludges from electroplating operations), F007 (spent cyanide plating bath solutions from electroplating operations where cyanides are used in the process), F009 (spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process), F011 (spent cyanide solutions from salt bath pot cleaning from metal heat-treating operations), F012 (quenching wastewater treatment sludges from metal heat-treating operations where cyanides are used in the process), and F019 (wastewater treatment sludges from the chemical conversion coating of aluminum). A wastewater is defined as those wastes that contain less than 1 percent total organic carbon and less than 1 percent total suspended solids. Those wastes that do not meet these criteria are defined as nonwastewaters and thus would contain greater than or equal to 1 percent TOC, or greater than or equal to 1 percent total suspended solids. The technologies identified by EPA as BDAT for these

listed wastes include alkaline chlorination, followed by precipitation, filtration, and stabilization of metals for Waste Code FC06 (nonwastewaters only); and electrolytic oxidation followed by alkaline chlorination, followed by precipitation, settling, filtration, and stabilization of metals for F012. The technology identified as BDAT for Waste Codes F007, F009, and F011 is alkaline chlorination, followed by precipitation, settling, and sludge dewatering. Concentration-based treatment standards for F006 wastewaters and F019 will be promulgated with the "Third-Third" wastes on May 8, 1990. Until that time, cyanide-bearing F006 wastewaters and F019 wastes are subject to the "soft-hammer" provisions.

With the exception of noncyanide-bearing F006 and F019 wastes [which were included in the "First-Third" category (53 FR 31152)], F006 wastewaters, and cyanide-bearing F019 wastes, the electroplating wastes discussed in this report (F006, F007, F009, F011, and F012) were all included in the "Second-Third" listed waste category (54 FR 26594).

Tables A-2 through A-5 list the BDAT treatment standards for each of these wastes.

TABLE A-2. BDAT TREATMENT STANDARDS, METAL-FINISHING LIQUIDS SUBCATEGORY FOR F007 AND F009 (NONWASTEWATERS)

	Maximum for any single grab sample	
Constituent	Total composition, mg/kg	TCLP, mg/L
Cyanides (total)	590	a
Cyanides (amenable)	30	a
Cadmium	a	0.066
Chromium	a	5.2
Lead	a	0.51
Nickel	a	0.32
Silver	a	0.072

[a] Not applicable

TABLE A-3. BDAT TREATMENT STANDARDS, METAL-FINISHING LIQUIDS SUBCATEGORY FOR F006, F007, AND F009 (WASTEWATERS)

Constituent	Maximum for any single grab sample (total composition, mg/kg)
Cyanides (total)	1.9
Cyanides (amenable)	0.1
Chromium	0.32
Lead	0.04
Nickel	0.44

TABLE A-4. BDAT TREATMENT STANDARDS, METAL-FINISHING LIQUIDS SUBCATEGORY FOR F011 AND F012 (NONWASTEWATERS)

Constituent	Maximum for any single grab sample	
	Total composition, mg/kg	TCLP, mg/L
Cyanides (total)	110	a
Cyanides (amenable)	9.1	a
Cadmium	a	0.066
Chromium	a	5.2
Lead	a	0.51
Nickel	a	0.32
Silver	a	0.072

[a] Not applicable.

TABLE A-5. BDAT TREATMENT STANDARDS, METAL-FINISHING LIQUIDS SUBCATEGORY FOR F011 AND F012 (NONWASTEWATERS)

Constituent	Maximum for any single grab sample (total composition, mg/kg)
Cyanides (total)	1.9
Cyanides (amenable)	0.1
Chromium	0.32
Lead	0.04
Nickel	0.44